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THE SETTING OF PLASTER OF PARIS

BY HARRY B. WEISER AND FERRIN B. MORELAND

The setting of plaster of Paris involves a definite chemical transformation from the hemihydrate to the dihydrate of calcium sulfate. Since the former is 4.5 times as soluble as the latter[1] at room temperature, Le Chatelier[2] assumed the following mechanism for the setting process: The hemihydrate first forms a saturated solution in water, then reacts to form the dihydrate giving a supersaturated solution of the latter from which is deposited a compact mass of interlacing needle-shaped crystals—the set plaster.[3] The amount of water necessary to bring the hemihydrate back to the fully hydrated condition is much less than is necessary to dissolve it since a given amount of solution supersaturated with respect to gypsum, deposits crystals of the latter, thereby releasing the water to dissolve another portion of hemihydrate—the process continuing until the transformation to gypsum is complete.

For more than a quarter of a century Le Chatelier's theory of the mechanism of the setting of plaster of Paris was regarded as completely satisfactory. But in more recent years it has been considered by a number of investigators as inadequate to account for all the facts. Following the lead of W. Michaelis[4] and Keisermann[5] who observed the formation of a jelly as well as of crystals in the setting of Portland cement, they have visualized the formation of some kind of a jelly as an intermediate stage in the setting of plaster of Paris. Thus, Cavazzi[6] observed that gypsum precipitated rapidly from aqueous solution with alcohol gave a gelatinous mass from which distinct crystals separated on standing. Without further evidence, he concluded that there was probably an intermediate gel stage in the setting of plaster.

Traube[7] was the next to suggest that colloidal behavior plays a role in the setting process. It is a well-known fact that soluble salts may have a marked effect on the setting rate,[8] some salts accelerating it and others retarding it. To account for this behavior Rohland[9] assumes, in accord with Le Chatelier's theory, that any salt which increases the solubility of calcium sulfate will accelerate the setting while any salt which decreases the solubility will retard the setting. This explanation is inadequate since small amounts

[1] Marignac: Ann. Chim. Phys., (5) 1, 274 (1874).

[2] "Recherches experimentales sur la constitution des mortières hydrauliques," Paris (1887); cf., also, van't Hoff et al: Z. physik. Chem., 45, 257 (1903); Rohland: Z. anorg. Chem., 31, 437 (1902); 35, 194; 36, 332 (1903); Jolibois and Chassevent: Compt. rend., 177, 113 (1923).

[3] Cf., also, Chassevent: Ann. Chim., 6, 244 (1926).

[4] Chem-Ztg., 17, 982 (1893); Kolloid-Z., 5, 9 (1909); 7, 320 (1910).

[5] Kolloidchem. Beihefte, 1, 423 (1910).

[6] Kolloid-Z., 12, 196 (1913); cf. Neuberg and Rewald: 2, 354 (1908).

[7] Kolloid-Z., 25, 62 (1919).

[8] Ditte: Compt. rend., 126, 694 (1898).

[9] Z. Elektrochemie, 14, 421 (1908).

of soluble sulfates decrease the solubility of gypsum and yet increase the rate
of set.   And there are other exceptions.[1]   Traube observed the effect of salts
on the time required for the plaster to attain a definite state of hardness.
He found cations to be especially important, the order of influence being the
reverse of that in which they precipitate sols.   This led him to the conclusion,
which is not obvious, that there must be some kind of colloidal behavior in-
volved in the setting process.

Ostwald and Wolski[2] likewise concluded from indirect evidence that
colloidal processes are probably involved in the setting of plaster of Paris.
Experimentally, they followed the rate of change in viscosity of suspensions
of plaster, varying the concentration of the suspensions, the degree of dis-
persion, the temperature and the nature of the medium, i. e., using solutions
of various salts as well as pure water. The theoretical deductions from the
experimental data were promised in a second paper which was never published.
They merely state that the viscosity data indicate a colloid process, "as for
example, the separation of perhaps only a thin gel layer as an integral part
of the setting process."

The guarded statement of Ostwald and Wolski that "perhaps only a thin
gel layer" was formed at some stage of the setting process together with their
failure to discuss theoretically their viscosity data suggests that they were
probably in doubt as to whether there was any gel formation at all.   In marked
contrast to this Baykoff,[3] Neville[4] and Budnikoff[5] come out definitely in
support of the formation of a gel as an intermediate stage in the setting proc-
ess.   Baykoff reached this conclusion as a result of a procedure which he
claimed would give a gypsum jelly. Five to ten grams of hemihydrate were
mixed with 100 cc of water and shaken vigorously.   On stopping the shaking
after a suitable time, the entire mass was said to set to a "gelatinous mass
presenting the appearance of a silica gel."   The setting took place in 2 or 3
minutes if a 10 percent solution of potassium or ammonium sulfate was used
instead of pure water.   This behavior will be considered in the experimental
part of this paper.

Since the hydration of plaster of Paris is an exothermic reaction, the rate
of the reaction may be followed by measuring the rate of evolution of heat.
This has been done by Cloez,[6] Emley,[7] Chassevent,[8] Neville,[9] Budnikoff,[10]
Hansen[11] and others. Starting with a high grade of hemihydrate mixed with
pure water and determining the rise in temperature with time, an S-shaped

[1] Haddon: J. Soc. Chem. Ind., 165T, (1920); 122T (1921); cf. Welch: J. Am. Ceramic
Soc., 6, 1197 (1923).
[2] Kolloid-Z., 27, 79 (1920); Neugebauer: 31, 40 (1922).
[3] Compt. rend., 182, 129 (1926); In article by Budnikoff: Kolloid-Z., 42, 151 (1927).
[4] J. Phys. Chem., 30, 1037 (1926).
[5] Kolloid-Z., 42, 151 (1927); 44, 242 (1928).
[6] Bull., (3) 29, 171 (1903).
[7] Trans. Am. Ceram. Soc., 19, 573 (1917).
[8] Ann. Chim., 6, 264 (1926).
[9] J. Phys. Chem., 30, 1037 (1926).
[10] Kolloid-Z., 44, 242 (1928).
[11] Ind. Eng. Chem., 22, 611 (1930).

curve is obtained. For an interval of several minutes the temperature rises but slightly, after which it goes up relatively rapidly to a maximum and then falls off. Neville observed that a so-called "initial set"[1] results before there is any marked heat evolution. He concluded from this that the setting process takes place in two stages: (1) the formation of a gel or adsorption complex between the plaster and water, a process accompanied by but little heat effect and (2) the exothermic reaction between the plaster and the adsorbed water, forming gypsum. At first he attributed the observed contraction in volume to the initial step and the subsequent expansion to the second step, but later[2] he concluded that the hydration which causes the initial contraction takes place throughout the whole period but it is masked for a time by the thermal expansion.[3] The effect of salts on the rate of setting was attributed to their effect on the adsorption of water to form a gel and subsequently to their catalytic action on the reaction between hemihydrate and water.

Budnikoff carried out thermometric observations on the rate of setting of plaster under varying conditions, apparently quite independent of the work of Neville and reached similar conclusions as to the mechanism of the process. There is a distinct difference in the form of Neville's time-temperature curves and those obtained by Budnikoff since the latter, apparently without knowing it, used a plaster containing a large amount of soluble anhydrite. Accordingly there was a marked rise in temperature of 15° to 20° at the outset as a result of the hydration of the anhydrite to hemihydrate.[4] Budnikoff goes a step further than Neville and postulates the formation of a gel around the plaster particles which protects them from the action of water thereby producing the induction period which varies in length depending on the nature of the addition agents present. The period of induction is assumed to be broken by crystallization of the enclosing gel which allows the water to again act on the plaster. This theory deserves little consideration, for if the facts are as postulated the disappearance of the first gel layer would merely be followed by the formation of a new one giving a second induction period, and so on, the process being repeated indefinitely.

The arguments for gel formation as a step in the setting of plaster of Paris may seem quite conclusive if taken collectively. Indeed one of us[5] but a short time ago was distinctly impressed by the conclusions of Neville. On reflection it appears, however, that all the evidence of true gel formation is indirect. No one, not even Baykoff, as we shall see, has really observed the formation of a gel of gypsum prior to the appearance of the interlacing crystals in the plaster pastes. Chassevent[6] independently of Neville or Budnikoff observed an initial inhibition period in the time-heat curves for the hydration of hemihydrate. It probably never occurred to him to invoke the formation

[1] Cf., however, Emley: Trans. Am. Ceramic Soc., 19, 573 (1917).
[2] Colloid Symposium Monograph, 6, 309 (1928).
[3] Cf. Williams and Westendick: J. Am. Ceramic Soc., 12, 381 (1929).
[4] Cloez: Bull., (3) 29, 171 (1903); Chassevent: Ann. Chim., 6, 265 (1926) .
[5] Weiser: "The Colloidal Salts," 199 (1928).
[6] Ann. Chim., 6, 264 (1926).

of a gelatinous adsorption complex to account for this period of inhibition since he had previously observed an inhibition period in the crystallization of gypsum from its supersaturated solution in the absence of nuclei. Indeed he found that solutions of gypsum containing 5 times the saturation value did not start to crystallize for 28 minutes when particular care was taken to exclude nuclei. The effect of salts on the rate of setting was also observed. In the case of potassium sulfate he states that this "accelerates the crystallization and diminishes the time interval during which the instable saturated solutions of hemihydrate remains without crystallization."

Hansen[1] likewise failed to find any direct evidence of gel formation and apparently independent of Chassevent, reached the same conclusion as the latter that "the effect of foreign material upon the rate of precipitation from its supersaturated solution appears to explain the ability of foreign materials to accelerate or retard the setting of calcined gypsum pastes."

While one can offer no objections to the statements of either Chassevent or Hansen, their conclusion in the last analysis is merely that foreign substances influence the rate of set by influencing the rate at which gypsum precipitates from its supersaturated solution. On the other hand, they offer no explanation of the variation in behavior with various substances. Chassevent does say that substances which increase the sulfate ion concentration accelerate the crystallization; but as we shall see this is not necessarily true.

This communication deals with thermometric and optical observations of the hydration of plaster of Paris under widely varying conditions with the end in view (1) of throwing light on the existence or non-existence of gel formation as a stage in the setting process and (2) of formulating a general theory to account for the effect of addition agents on the rate of setting.

The Question of Gel-Formation in the Setting of Plaster of Paris

1. *Baykoff's gypsum "gel."* As pointed out in the previous section, Baykoff claims to get gypsum as a "gelatinous mass presenting the appearance of a silica gel" by precipitation of the gypsum from a supersaturated solution in water or ammonium sulfate solution. His procedure using an ammonium sulfate solution was repeated: Ten grams of ammonium sulfate were dissolved in 100 cc of water in a 250 cc stoppered bottle and to this was added 10 grams of plaster of Paris. After shaking at intervals, rapidly at first and then more gently for approximately 2 minutes and allowing to stand quietly, it was noted that the mixture gradually became somewhat rigid so that the bottle could be turned upside down without the mass flowing. This was obviously the gypsum "gel" to which Baykoff referred. It possessed but little rigidity and broke completely on gentle stirring and did not reset on standing. Microscopic examination showed it to be a network of relatively long crystal needles of gypsum. The experiment was repeated withdrawing samples of the mixture for microscopic examination at intervals of 30 seconds. After 1.5 to 2 minutes the appearance of myriads of small needles was a reminder that the mixture

[1] Ind. Eng. Chem., **22**, 611 (1930).

should be allowed to stand quietly if a "gel" was desired. If the shaking was continued the mass did not "set." The only point of resemblance between this cloudy, non-uniform entangling mass of crystal needles and silica gel is that both stay in the containing vessel when the latter is inverted. Silica gel or jelly, like all true jellies, consists of myriads of ultramicroscopic particles that have adsorbed the solvent strongly and have become enmeshed into a network that entrains liquid.[1] A mass of relatively coarse crystal needles that entangles water constitutes what Holmes[2] has called a "false gel" in contra-distinction to the true gels where the structure is ultramicroscopic. Thus if one dissolves 4–5 grams of caffeine in 100 cc of boiling water and allows the solution to cool slowly, the beaker may be inverted without loss of water. In this case, as in the case of the gypsum, the structure consists of compara-tively coarse needle crystals. Everybody is agreed that in the process of setting, plaster of Paris gives an enmeshing network of gypsum needles that entrains the excess water. If this is what people mean when they say that gelation is a step in the setting of plaster of Paris, then one will not question the statement. But this is not what they mean. Neville assumes specifically that the gel is an adsorption complex between the water and the plaster which forms without any chemical change. Budnikoff has the same idea, for he speaks of the initial formation around the plaster particles of a gel layer which subsequently crystallizes.

2. *The Effect of Gypsum Nuclei on the Rate of Set of Plaster of Paris.* It is a well-known fact that samples of high-grade plaster of Paris free from any added accelerators or retarders show considerable variation in the time of set. In general a plaster which exhibits a long period of inhibition before there is any marked rise in temperature, is designated as a slow-setting plaster while one with a short period of inhibition is referred to as a rapid-setting plaster. If the period of inhibition is due to the building up of an adsorption complex "whereby the two reactants are brought into chemical contact," as Neville assumes, then it is not obvious why different samples prepared by similar procedures and having the same average particle size, should show such differ-ences in the period of inhibition. On the other hand, if the inhibition period is merely a phenomenon of supersaturation, the variation in the length of the period with different samples of plaster might well be due to variation in the number of gypsum nuclei in the samples. Chassevent[3] showed that the addition of gypsum to plaster hastened the time of set and Hansen[4] found that if a plaster paste was made with water shaken for 35 minutes with a small amount of plaster which ordinarily attained its maximum temperature in 75 minutes, the time of setting was appreciably shortened.[5] But the importance of the presence of gypsum nuclei in plaster of Paris on the rate at which it sets has been pretty generally overlooked especially by everybody who has visualized gel formation as a stage in the setting process.

[1] Weiser: Bogue's "Colloidal Behavior," 1, 393 (1924).
[2] Colloid Symposium Monograph, 1, 24 (1923).
[3] Ann. Chim., 6, 313 (1926).
[4] Ind. Eng. Chem., 22, 611 (1930).
[5] Cf. Wiggin's Sons Co., British Pat., 221,853 (1923).

In this as in succeeding experiments on the rate of set of plaster, the thermometric method was employed. A diagram of the apparatus used is shown in Fig. 1. This consists of a Dewar vacuum vessel 8.2 cm internal diameter and 29 cm deep. The vessel is supplied with a snug-fitting cork stopper attached to a board which rests on the top of the vessel when the stopper is inserted. To the stopper is suspended firmly a cork ring which holds the paraffined paper cup containing the plaster paste. A hole through the center of the stopper admits a 100° thermometer graduated in tenths of a degree.

The procedure using this apparatus is as follows: Into a 130 cc paraffined paper cup is measured exactly 35 cc of distilled water kept in the thermostat at 25°. A 50-gram sample of the plaster likewise kept at 25° was put into the cup and the stop-watch started. By brisk stirring for 10 seconds with a glass rod, a uniform paste was obtained. The cup with contents was put in the holder, the thermometer inserted in the paste which was then covered with a thin layer of paraffine oil to prevent evaporation. After placing in the Dewar vessel, the temperature was read at 1 minute intervals until after the maximum temperature was attained and the temperature began to fall regularly.

The plaster of Paris used in these experiments was a high grade product secured from the Central Scientific Company. The rate of set of the plaster was somewhat too rapid but it was found that this was decreased by ignition. Accordingly 2-kilogram samples in a flat tin container were placed in an electric oven at 130° for two hours, stirring thoroughly every 30 minutes. Approximately 40 kilograms were treated in this way and the entire amount was spread out thinly on paper in a closed room in which the humidity was kept high. This served to transform into hemihydrate any anhydrite that was formed during the ignition.

FIG. 1
Diagram of Calorimeter.

After thorough mixing, following the standard procedure,[1] the plaster was transferred to tightly corked bottles. Unless otherwise stated this "Standard Sample" was used in all experiments described herein.

The time-temperature curves were run on (1) a sample of the original plaster that had been heated at 130° for 5 hours and allowed to stand in the air over night, (2) on the standard sample described above, and (3) on the

[1] Treadwell-Hall: "Analytical Chemistry," **2**, 53 (1924).

standard sample to which varying amounts of gypsum were added. The gypsum used was set plaster which was finely ground to pass a 100 mesh sieve. The weighed sample was thoroughly mixed with the 50 gram weight of plaster before the water was added. The time-temperature curves for various mixtures given in Table I are shown in Fig. 2.
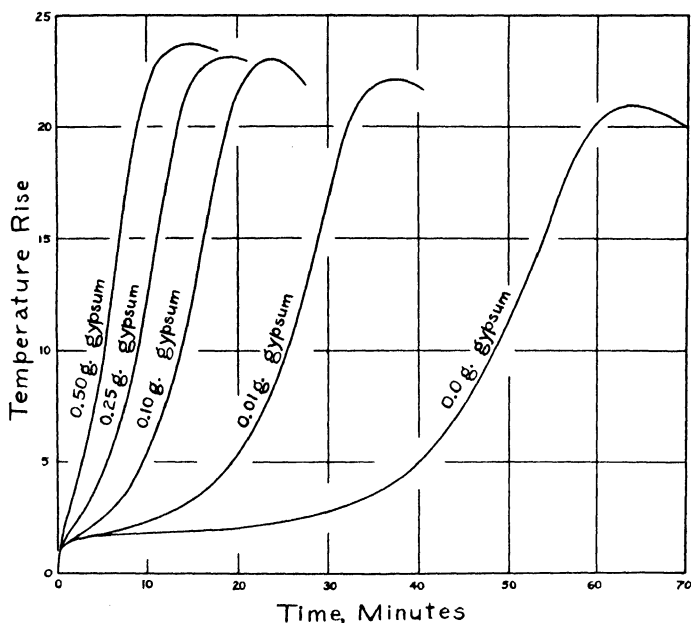
FIG. 2
Time-Temperature Curves obtained with Different Samples of Plaster of Paris.

TABLE I

Observations on Different Samples of Plaster of Paris

| Substances mixed with 35 cc water | | | Time to attain | Tensile strength | |
| Plaster of Paris | Grams gypsum | | maximum | pounds per square inch | |
50 grams	added	calculated	temperature	after 1 day	after 10 days
Sample heated 5 hours	0.0	0.00012	100.0		
Standard sample	0.0	0.00092	64.0	235	490
Standard sample	0.01	0.0098	38.0		
Standard sample	0.05	0.052	26.5		
Standard sample	0.10	0.08	24.0		
Standard sample	0.25	0.23	19.0		
Standard sample	0.50	0.50	16.0	300	450
Standard sample	1.00	0.94	14.0		

From the form of the curve with a plaster to which no gypsum was added it will be noted that there is a sharp rise of approximately 1° which is probably due to heat of wetting and to the transformation of any anhydrite into hemihydrate. The initial rise is followed by a "period of inhibition" after which

there is a gradual increase in rate of reaction until a maximum temperature is
attained. The sample heated for 5 hours (curve not shown) which was quite
free from nuclei did not attain the maximum temperature for 100 minutes
while the standard sample showed a shorter inhibition period and reached the
maximum temperature in 65 minutes. The inhibition period was appreciably
cut down by adding nuclei of gypsum until with 0.5 gram in 50 grams of
plaster, it was practically zero. When the time to attain the maximum tem-
perature is plotted against the weight of gypsum nuclei added a parabolic
curve is obtained, Curve I, Fig. 3, which shows that the rate of set approaches
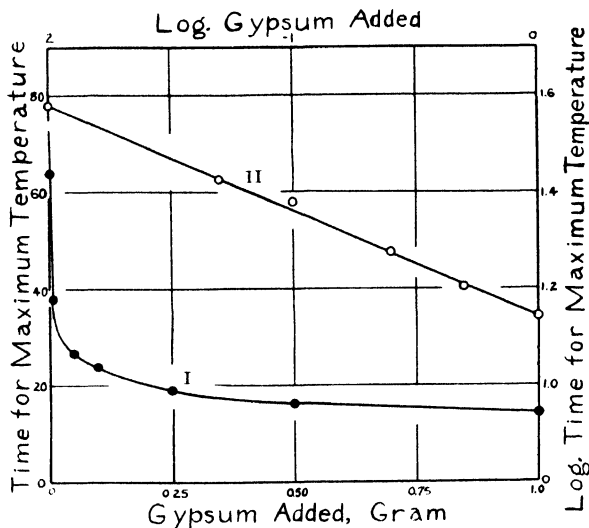
Fɪɢ. 3
Effect of the addition of Gypsum Nuclei on the Rate of Set of Plaster of Paris.

infinity as the number of nuclei present approaches zero. Plotting the data
on logarithmic coordinates the straight line, Curve II, of Fig. 3, is obtained.
The equation for the curve is $W = 1.52 \times 10^5 t^{-4.55}$, where W = grams gypsum
added and t = time to attain maximum temperature. From this the values
for the weight of nuclei added may be calculated. For the purposes of com-
parison with the actual amounts added, the calculated values, which show
close agreement, are given in the third column of Table I. Using the equation,
the amount of nuclei present in the two samples to which no gypsum was added
can be calculated. It is interesting to note that the calculated value for the
very slow setting plaster is approximately 0.0001 gram per 50 grams while
for the standard sample it is less than 0.001 gram per 50 grams.

The above observations indicate that the length of the inhibition period
is influenced to a marked degree by the amount of gypsum nuclei in the plaster
paste after the mixing with water is complete. Hence the observed inhibition
period appears to result from delayed precipitation from a supersaturated
solution owing to dearth of nuclei rather than to the time necessary to form
a gel or adsorption complex.

It cannot be too strongly emphasized that the period of inhibition even in a relatively slow setting plaster, is not a period of rest so far as chemical change is concerned. The temperature rises gradually throughout the entire period, showing the precipitation of more and more gypsum on nuclei already present and the formation of new nuclei until there is rapid precipitation of gypsum followed by further solution and hydration of hemihydrate throughout the mass. This was confirmed by a motion picture record of the process magnified 30 times. The absence of temperature rise, or an actual drop in temperature, during the first stages of the process, is due either to loss of heat by evaporation of water from the paste or radiation owing to insufficient insulation in a room where the temperature is lower than that of the newly prepared paste.

In view of the fact that there is a gradual increase in the viscosity of the plaster paste from the time of its formation, it is not possible to indicate any one point where the plaster begins to harden and to designate it as the "initial set." Emley[1] states specifically that none of the methods such as measurements of expansion or of temperature rise, is capable of indicating an "initial set."

In the last two columns of Table I are given the tensile strengths,[2] after 1 day and after 10 days, of the standard plaster with and without the addition of a small amount of gypsum. It will be noted that the unseeded sample which sets slowly and the seeded sample which sets rapidly, attain approximately the same strength after 10 days; but the rapid-setting sample has a higher strength after 1 day than the slow-setting sample. It would seem from these observations that suitable ignition to eliminate gypsum nuclei is all that is necessary to obtain slow-setting plaster of Paris and that the rate of set can be increased to any desired point by seeding with a suitable amount of finely powdered gypsum.

3. *Effect of stirring Plaster-Water Mixtures on the Rate of Set.* It is a well-known fact that stirring a mixture which has the property of setting to a uniform jelly structure will prevent or at least greatly retard the gel formation. If the setting of plaster of Paris involves the initial formation of a jelly, it would follow that the process and the subsequent set would be retarded by agitation of the plaster-water mixture. On the other hand, if the phenomenon consists merely of dissolution and hydration of hemihydrate followed by precipitation of gypsum from its supersaturated solution, and the usual period of inhibition is due to a scarcity of gypsum nuclei, it would follow that stirring would tend to break down the supersaturated solution, supplying nuclei which would decrease the length of the induction period and hence the time of set. As a matter of fact, the latter is what happens as the following experiments show. Fifty-gram samples of the standard plaster were mixed rapidly with 35 cc of water in a paraffined paper cup. The pastes were subjected to rapid agitation for varying periods of time, using a Central Scientific Company motor-driven stirrer No. 12860 running at maximum speed. The stirrer was a metal disc of 6 paddles, 3 cm. in diameter. The time-temperature curves

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[1] Trans. Am. Ceramic Soc., **19**, 573 (1917).

[2] Determined by the standard procedure of the American Society for Testing Materials.

obtained in the usual way for the several samples are reproduced in Fig. 4. Note especially the shortening of the inhibition period with increasing time of stirring. A lower maximum temperature was recorded for the mixtures stirred 3 and 4 minutes than for those stirred a shorter time because of loss of heat before placing the mixture in the calorimeter. The results are summarized in Table II and shown graphically in Fig. 5. It is significant that the form of the curve is similar to that obtained by the direct addition of varying amounts of gypsum to the plaster.
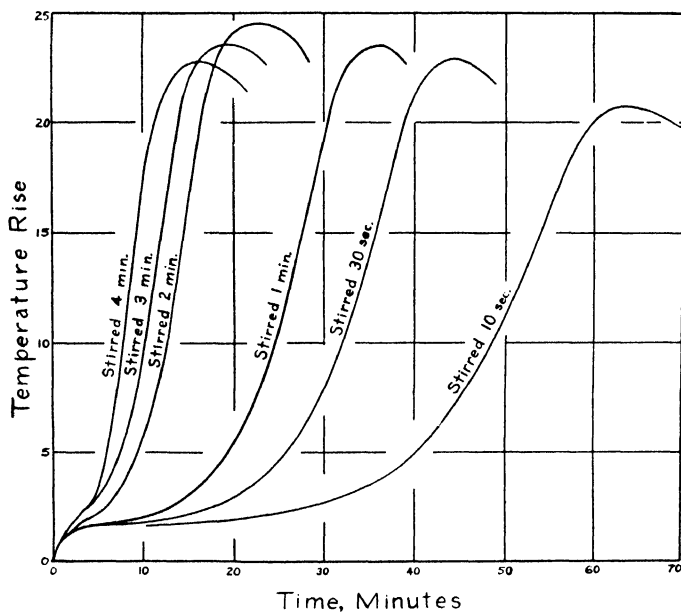
FIG. 4
Time-Temperature Curves for Plaster of Paris Pastes Stirred for Varying Periods.

TABLE II

Effect of Stirring on the Rate of Set of Plaster of Paris

Time of stirring with motor driven stirrer	Time for maximum temperature
10 seconds (by hand)	64
30 seconds	44
1 minute	36
2 minutes	22
3 minutes	19
4 minutes	17
5 minutes	Set before the thermometer was introduced

These three sets of observations individually and collectively furnish strong evidence in support of the view that the inhibition period is a phenomenon of supersaturation rather than of gel formation.
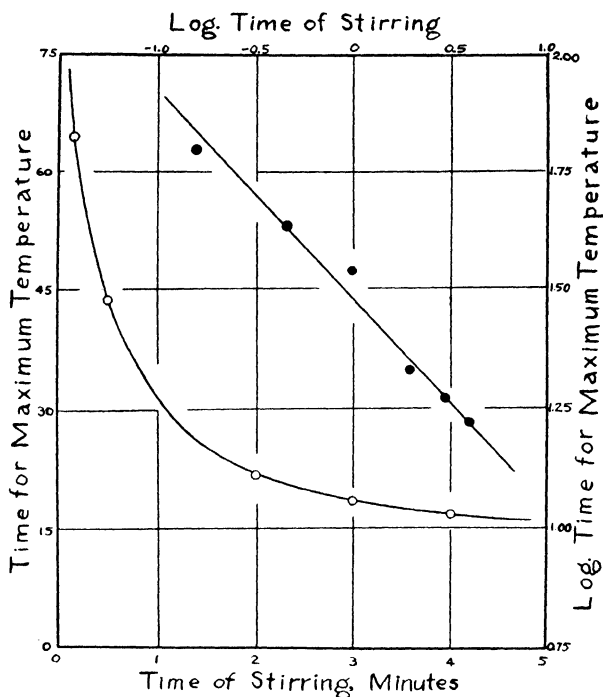
FIG. 5

Effect of Time of Stirring on the Rate of Set of Plaster of Paris.

Effect of Foreign Electrolytes on the Rate of Setting of Plaster of Paris

Since the setting of plaster of Paris involves the precipitation of gypsum from its supersaturated solution, the effect of electrolytes on the process may be considered in the light of von Weimarn's theory of the precipitation process.[1] Von Weimarn calls attention to the fact that there are a number of factors on which precipitation depends, the most important of which are (1) the solubility of the precipitating substance and (2) the concentration at which the precipitation begins. The process of precipitation is considered as taking place in two stages: the first stage in which the molecules condense to invisible or ultramicroscopic particles; and the second, which is concerned with the growth of the particles as a result of diffusion.

Considering the first stage, the velocity W at the first moment can be formulated

$$W = K \frac{\text{precipitation pressure}}{\text{precipitation resistance}} = K \frac{Q - L}{L} = K \frac{P}{L} = KU$$

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[1] "Zur Lehre von den Zuständen der Materie" (1914).

in which K is a constant, Q the total concentration of the substance that is to precipitate and L the ordinary solubility of the substance. $Q - L = P$, the amount of supersaturation and $P/L = U$, the percentage supersaturation. A given value of U will result either from a large P value or a small L value. In the first case a large amount of precipitate will be thrown down in a given time while in the second a relatively small amount will form.

The velocity V of the second stage of the process is given by the Nernst-Noyes equation

$$V = D/S \cdot O \cdot (Q - L)$$

where D is the diffusion coefficient, S the length of the diffusion path, O the surface, Q the concentration of the surrounding solution and L the solubility of the dispersed phase for a given degree of dispersity. As in the von Weimarn equation $Q - L$ is the absolute supersaturation.

This general statment of the conditions which obtain during precipitation from solution may now be applied to the precipitation of gypsum from its solution both in the presence and in the absence of foreign electrolytes. The solubility of plaster of Paris in water is approximately 0.067 mol per liter[1] and when this hydrates to gypsum which has a solubility of but 0.015 mol per liter, the percentage supersaturation is $\dfrac{0.067 - 0.015}{0.015} = 3.5 = U$. The initial velocity of precipitation is proportional to U, that is, $W = K\,3.5$. In view of the relatively long period of inhibition following the mixing of pure plaster of Paris with water, it is obvious that this percentage supersaturation is insufficient to cause rapid precipitation of nuclei which must be present in abundance for a rapid reaction to take place throughout the mass. Now if the addition of a foreign electrolyte cuts down the period of inhibition it follows that the percentage supersaturation of the solution with respect to gypsum must be greatly increased. This may be accomplished in one of two ways: Either the solubility of the hemihydrate is increased appreciably more than that of gypsum by the presence of the foreign electrolyte or the solubility of the gypsum is decreased appreciably more than that of hemihydrate by the presence of the foreign electrolyte. In the first instance the value of $(Q-L)/L = P/L$, the percentage supersaturation, is increased because the value of Q, which is determined by the solubility of hemihydrate is increased proportionately more than L the solubility of the gypsum in the medium; and in the second case P/L is increased because L is decreased proportionately more than P in the given medium. In other words for a foreign electrolyte to change the initial rate of formation of nuclei as compared to the rate of formation in water alone, all that is necessary, other things being equal, is for the ratio of the solubility of hemihydrate to the solubility of gypsum to be greater or less than 4.5, the ratio of the solubilities in pure water. There is of course no reason to expect a constant ratio of solubilities in widely different environments but direct evidence of such variation in the solubility ratios are quite impossible to get in most cases since solutions of foreign electrolytes added to hemi-

[1] Marignac: Ann. Chim. Phys., (5) 1, 274 (1874).

hydrate usually result in such rapid precipitation of gypsum that the solubility of hemihydrate in the solution cannot be determined accurately. On the other hand, the observations recorded in the subsequent paragraphs furnish strong indirect evidence of the expected variation in the solubility ratio and in one case this has been evaluated experimentally.

Coming back to the question of growth of particles on nuclei already present, the Nernst-Noyes formulation states that the velocity of growth is
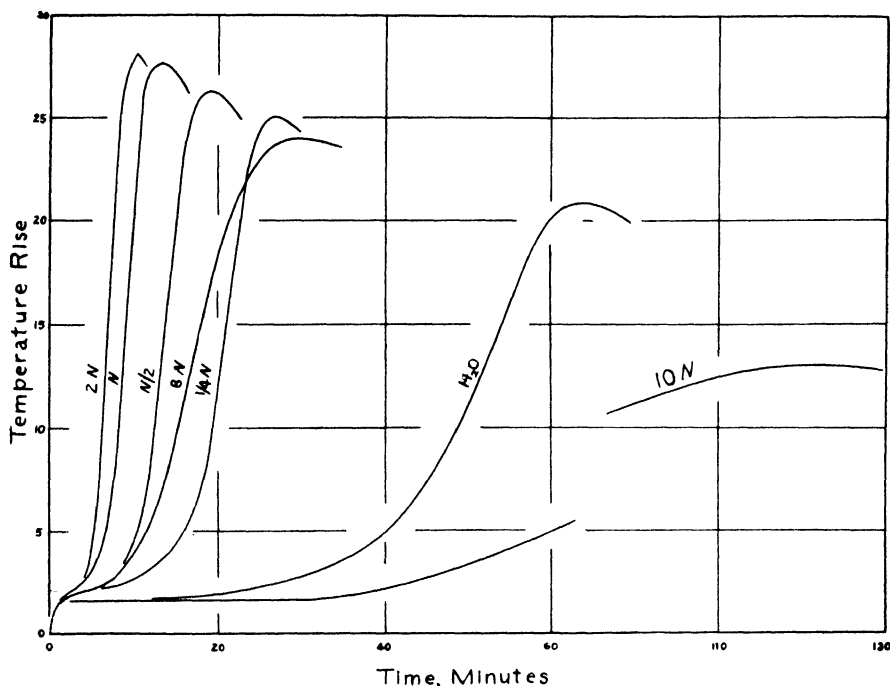
FIG. 6

Time-Temperature Curves for Mixtures of Plaster of Paris with Varying
Concentrations of NH_4NO_3.

proportional to $Q - L$, the absolute supersaturation. For a given amount Q in solution, the velocity of growth is influenced strongly by the solubility. If L is small, so that the $Q - L$ value is relatively large, the growth of particles will be relatively rapid; while if L is large so that $Q - L$ is relatively small, well formed crystals will form slowly. As is well known, for the growth of large well-formed crystals, the $Q - L$ value must be very small and there must be few nuclei on which precipitation takes place.

In the subsequent experiments the effect on the rate of set of plaster of Paris is determined for a few typical salt solutions and is considered in the light of the theory above outlined.

Effect of Ammonium Nitrate. Since ammonium nitrate is quite soluble and the solubility of gypsum in a wide range of concentration is known, the effect of this salt on the rate of set of plaster of Paris was first studied. Fifty-

gram portions of the plaster were mixed for 10 seconds with various concentra-
tions of salt solutions and the time-temperature curves obtained for the several
mixtures.   To give an idea of the way in which the form of the curve varies
with different concentrations of salt, a few of the curves are reproduced in
Fig. 6.   It is clear from these curves that for concentrations in the neighbor-
hood of 1 to 2 molar the inhibition period is very small and the rate of set is
quite rapid.   With concentrations below normal the inhibition period and the
rate of set become gradually longer approaching that of pure water.   The same
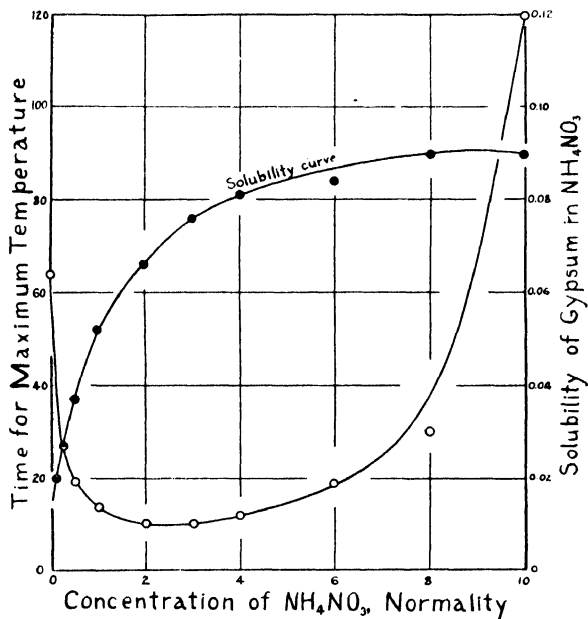
FIG. 7
Effect of the Concentration of NH_4NO_3 Solutions on the Rate of Set of Plaster of Paris.

is true for higher concentrations as evidenced particularly by the behavior in
10 normal solution where the period of inhibition is much longer than in pure
water and the time for the maximum temperature to be reached is twice as
long as in water.   The data are summarized in Table III and shown graphically
in Fig. 7.   The solubility curve of gypsum in ammonium nitrate solution[1]
is given for reference.   The U-shaped form of the rate of set curve indicates
that with low concentrations of nitrate solution, the ratio of the solubility of
hemihydrate to gypsum is sufficiently large that a high percentage super-
saturation of gypsum obtains.   This results in prompt precipitation of nuclei
and because of relatively high absolute supersaturation the growth of the
crystals goes on rapidly until the reaction is complete.   On the other hand, in
strong nitrate solution in which gypsum is quite soluble, $Q - L = P$ is small

[1] Cameron and Brown: J. Phys. Chem., 9, 210 (1905).

TABLE III

Effect of NH_4NO_3 on the Setting of Plaster of Paris

Concentration of NH_4NO_3 solution normality	Time for maximum temperature	Solubility of gypsum from curve of Cameron and Brown[1] Mol per liter	Tensile strength pounds/sq. in.	
			after 1 day	after 10 days
0.0	64	0.015	235	490
0.10	—	0.020	225	300
0.25	27	0.027		
0.5	19	0.037		
1.0	13.5	0.052	115	200
2.0	10.5	0.066		
3.0	10.0	0.076		
4.0	12.0	0.081		
6.0	19.0	0.084	60	40
8.0	30.0	0.089		
10.0	121.0	0.089	60	40

and P/L is small so that the initial formation of nuclei and the subsequent growth of crystals is greatly retarded.

The correctness of the above interpretation of the effect of varying concentrations of ammonium nitrate on the rate of set of plaster of Paris, is indicated further by optical observations of the form of the gypsum crystals obtained under varying conditions. The procedure was as follows. Exactly 1 milligram of the standard plaster was placed on a microscope slide and to this was added from a 2 cc graduated pipette, 0.1 cc of water or solution. After mixing, the sample was covered with a cover glass, taking care to avoid entrapping air bubbles. To prevent loss of water by evaporation, a film of paraffine was painted around the edge of the cover glass using a small camel's hair brush. After the transformation to gypsum was complete, a microphotograph of the resulting crystal was taken. Six of these photographs are reproduced in Fig. 8. Note that with relatively low concentration of NH_4NO_3, the needle crystals of gypsum are relatively fine. This means that the percentage supersaturation at the outset is so high that a great number of nuclei are formed and a relatively large number of small needles result. With increasing concentration of nitrate in which gypsum is more soluble, the percentage supersaturation at the beginning of the process falls off and the absolute supersaturation is reduced so that fewer, larger crystals result. This difference in size and shape of the crystals becomes quite marked in 6 N NH_4NO_3 and is particularly striking in 8 and 10 N NH_4NO_3. The very large crystals obtained in the 10 N NH_4NO_3 solution form quite slowly on few nuclei.

It should be remembered that for a complete quantitative formulation of the rate of formation and the nature of the precipitate as it is affected by the solubility of the substances concerned, it would be necessary to know the

[1]J. Phys. Chem., **9**, 210 (1905).

solubility of plaster of Paris in varying concentrations of ammonium nitrate throughout the range. It is obvious that such data cannot be secured with low concentrations of NH_4NO_3 because of the rapid rate of transformation of the hemihydrate to gypsum in the nitrate solution. On the other hand with 10 N NH_4NO_3 solution, the rate of transformation is relatively slow, so that it
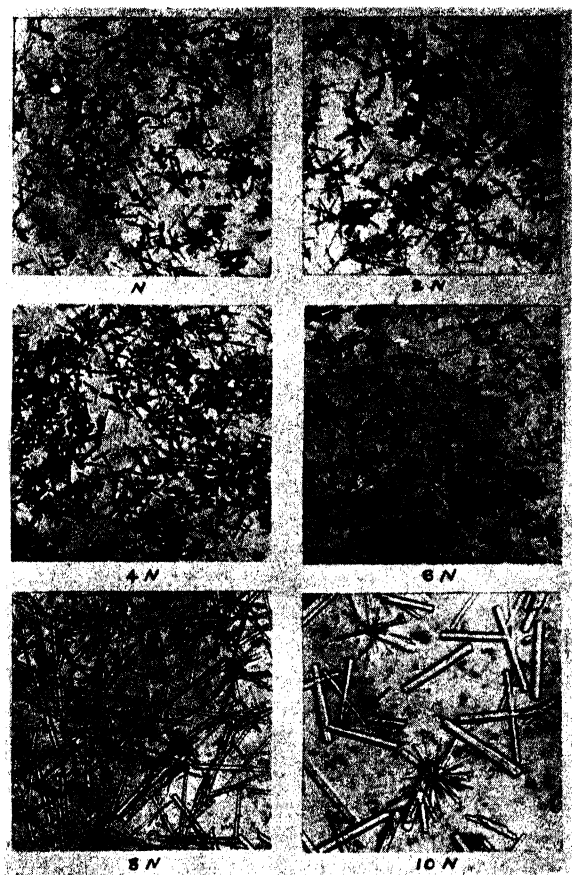
FIG. 8
Photomicrographs of Gypsum Crystals obtained in Various
Concentrations of NH_4NO_3 ($\times$ 40).

is possible to make a fairly accurate determination of the solubility of plaster of Paris in this solution. The procedure was as follows: approximately 10 grams of plaster was shaken for 5 minutes with 100 cc of 10 N NH_4NO_3. After centrifuging for a minute to throw down the excess plaster the solution was filtered rapidly through a Gooch crucible and a 50 cc portion of the filtrate heated to boiling and precipitated with $BaCl_2$ solution. After digesting hot over night, the precipitated $BaSO_4$ was collected in a Gooch crucible, ignited and weighed. On account of the contamination of $BaSO_4$ by adsorbed nitrate, the precipitate obtained was probably slightly heavier than it should have

been. However, the same procedure was used by Cameron and Brown[1] to determine the solubility of gypsum in nitrate solutions, so that the two determinations are comparable.

The solubility of plaster of Paris in 10 N NH_4NO_3 was found to be 15.5 grams $CaSO_4$ per liter or 0.114 mol per liter as compared with 0.089 mol per liter for the solubility of gypsum in the salt solution. The ratio of solubilities is thus 1.3 as compared with 4.5 in pure water and the $(Q-L)/L = P/L$ value in the nitrate solution is 0.3 as compared with 3.5 in pure water. These data furnish a quantitative basis for the above explanation of the observed differences in behavior of plaster of Paris in different solutions.
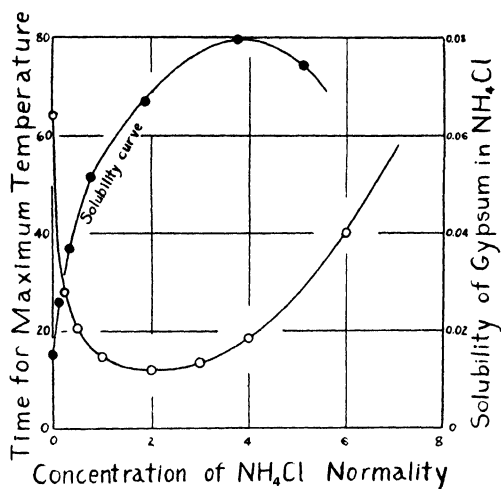
FIG. 9

Effect of the Concentration of NH₄Cl Solutions on the
Rate of Set of Plaster of Paris.

TABLE IV

Effect of NH₄Cl on the Setting of Plaster of Paris

Concentration of NH₄Cl solution normality	Time for maximum temperature	Solubility of gypsum from the curve of Cameron and Brown[1] Mols per liter
0.0	64	0.015
0.25	28	0.031
0.50	20.5	0.043
1.00	14.5	0.055
2.0	12.0	0.069
3.0	13.0	0.077
4.0	18.5	0.079
6.0	40.0	0.071

[1] J. Phys. Chem., 9, 210 (1905).

Referring to the last two columns of Table III, it will be seen that the tensile strength of the set plaster formed in the presence of NH_4NO_3 solutions is less than that formed in pure water. This is especially true when the nitrate solution is so strong that relatively few crystals of gypsum result.

Effect of Ammonium Chloride. The behavior of plaster of Paris in ammonium chloride solutions is essentially the same as with ammonium nitrate, as indicated by the results of the observations recorded in Table IV and shown graphically in Fig. 9. The curve has the same form as that obtained with nitrate but it runs slightly higher indicating that the initial percentage supersaturation with respect to gypsum is somewhat lower in the ammonium chloride than in the corresponding nitrate solutions. This was confirmed by a comparison of the microphotographs of the crystals obtained with like concentrations of the electrolytes.

Effect of Ammonium Sulfate. The effect of varying concentrations of ammonium sulfate on the rate of transformation of hemihydrate to gypsum is shown by the results tabulated in Table V which have been plotted in Fig. 10. It will be noted that the rate of hydration of the plaster, as evidenced by the time for attaining the maximum temperature, is greater than that with equivalent solutions not only of NH_4Cl and NH_4NO_3 but of all the salts investigated. As has been frequently pointed out, this rapid rate of reaction is contrary to Rohland's theory which attributes the increased rate of set of plaster in salt solutions to the increase in solubility of gypsum in these solutions, since the solubility curve reproduced in Fig. 10 discloses a smaller solubility of gypsum in low concentrations of $(NH_4)_2SO_4$ solutions than in water. As a matter of fact, the effect of the salt on the solubility of gypsum is in itself altogether insufficient to explain the effect of the salt on the rate of hydration of plaster. The important thing is the ratio of the solubility of plaster to that

TABLE V

Effect of $(NH_4)_2SO_4$ on the Setting of Plaster of Paris

Concentration of $(NH_4)_2SO_4$ solution normality	Time for maximum temperature	Solubility of gypsum from curve of Sullivan[1] Mols per liter	Tensile strength pounds/sq. in.	
			after 1 day	after 10 days
0.0	64.0	0.015	235	490
0.25	18.0	0.011		
0.50	11.0	0.011		
0.75	8.0	0.013		
1.00	7.5	0.014	165	425
1.50	7.0	0.017		
2.0	6.5	0.019		
3.0	7.0	0.025		
4.0	8.0	0.028		
6.0	14.0	0.031	160	475
7.0	16.5	0.032	150	385
8.0	20.0	0.033		

[1] J. Am. Chem. Soc., **27**, 529 (1905).

of gypsum in a given concentration of the salt, since this ratio determines the initial percentage supersaturation which influences greatly the rate of formation of nuclei and the absolute supersaturation which determines the rate of growth. The form of the curve in Fig. 10 indicates that the ratio of solubility of plaster to gypsum is high even in relatively low concentrations of $(NH_4)_2SO_4$. This would account for the absence of a period of inhibition in the time-temperature curves since $(Q-L)/L$ would be large; and would account also for the rapid rate at which the reaction once started goes to completion since $Q-L$ would be relatively large. That such is the case would follow also from the
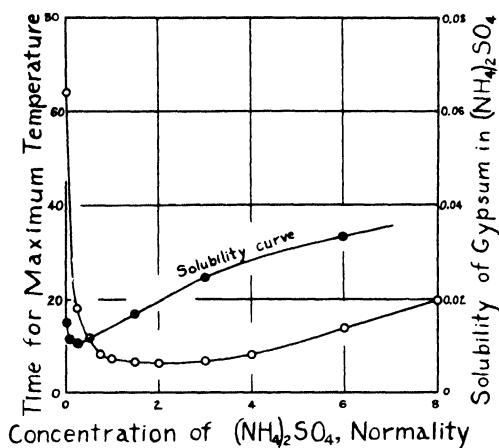
FIG. 10
Effect of the Concentration of $(NH_4)_2SO_4$ Solutions
on the Rate of Set of Plaster of Paris.

form of the particles obtained in the solutions of varying strengths, photomicrographs of which are given in Fig. 11. Note the relatively small size of the crystals formed in the zone of very rapid set in contact with solutions between N and $4N$. In $6N$ solutions the crystals which form somewhat slower are larger while in slightly higher concentrations a mat of long needles results. The lower $Q-L = P$ value and P/L value in solutions between 7 and $8N$ in which the solubility of gypsum is twice what it is in water, manifest themselves in a slower time of set and the formation of larger much longer needles.

The tensile strength data in Table V show that ageing the plaster which sets rapidly in the presence of sulfate gives a product which approaches in strength the product formed with pure water.

Effect of Ammonium Thiocyanate. Observations on the effect of NH_4CNS on the rate of formation of gypsum from plaster are summarized in Table VI. The curve representing the effect of the thiocyanate concentration on the time for attaining the maximum temperature is given in Fig. 12 together with similar curves for the other salts investigated. The photomicrographs of the gypsum crystals formed in the presence of varying concentrations of the salt
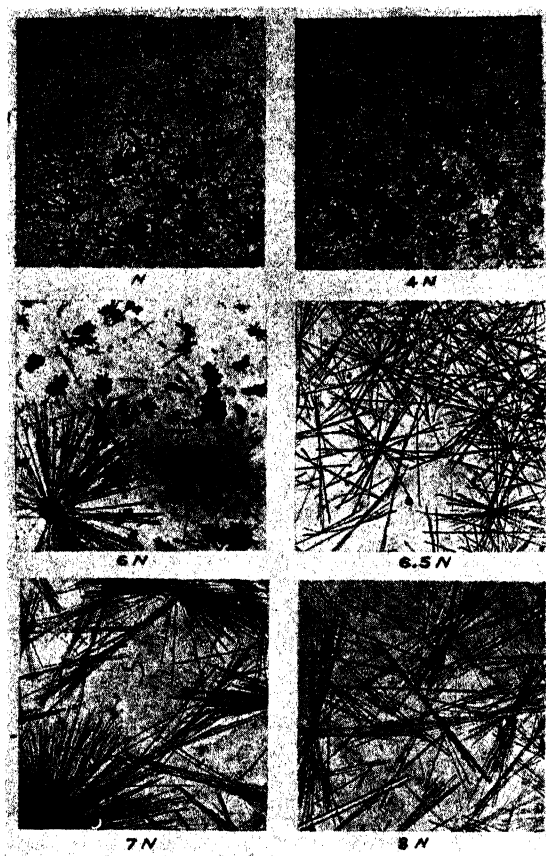
Fig. 11

Photomicrographs of Gypsum Crystals obtained in Various Concentrations of $(NH_4)_2SO_4$ ($\times$ 40).

TABLE VI

Effect of NH_4CNS on the Setting of Plaster of Paris

Concentration of NH_4CNS solution normality	Time for maximum temperature	Concentration of NH_4CNS solution normality	Time for maximum temperature
0.50	23.0	4.0	26.25
1.0	17.5	5.0	46.0
2.0	15.75	6.0	80.0
3.0	18.50		

are reproduced in Fig. 13. These data merely emphasize the importance of the degree of supersaturation on the rate of formation and the form of the crystals.

It is of interest to compare the crystal mass obtained in the presence of 6.5 N $(NH_4)_2SO_4$ with that formed in the presence of 6 N NH_4CNS. Although, at first glance they may appear quite similar, there is actually a distinct difference in the appearance as a result of a difference in the conditions leading to their formation. With the thiocyanate solution there was a marked period of inhibition in the time-temperature curve while with the sulfate solution there was little or no inhibition period. This indicates that
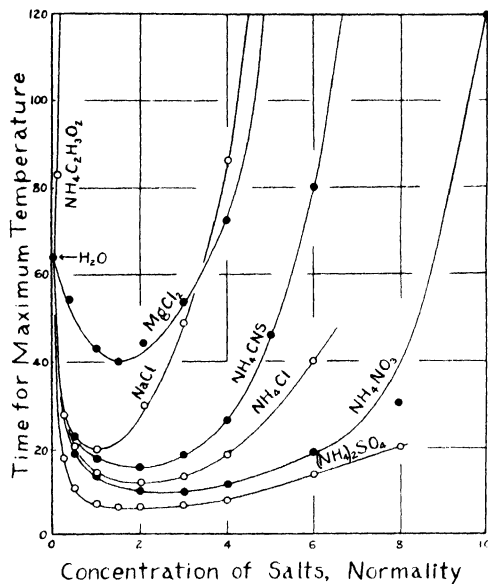
FIG. 12
Effect of Varying Concentrations of Several Electrolytes
on the Rate of Set of Plaster of Paris.

the percentage supersaturation is greater in the latter case. The actual supersaturation was also greater with $(NH_4)_2SO_4$ than with NH_4CNS since a very large number of fine needles formed rapidly with the former and a smaller number of thicker needles formed more slowly with the latter.

TABLE VII

Effect of NaCl on the Setting of Plaster of Paris

Concentration of NaCl solution normality	Time for maximum temperature	Solubility of gypsum from curves of Cameron.[1] Mols per liter
0.0	64	0.015
1.0	20	0.046
2.0	30	0.054
3.0	49.5	0.055
4.0	86	0.052
Saturated	251	0.040

[1] J. Phys. Chem., 5, 556 (1901).
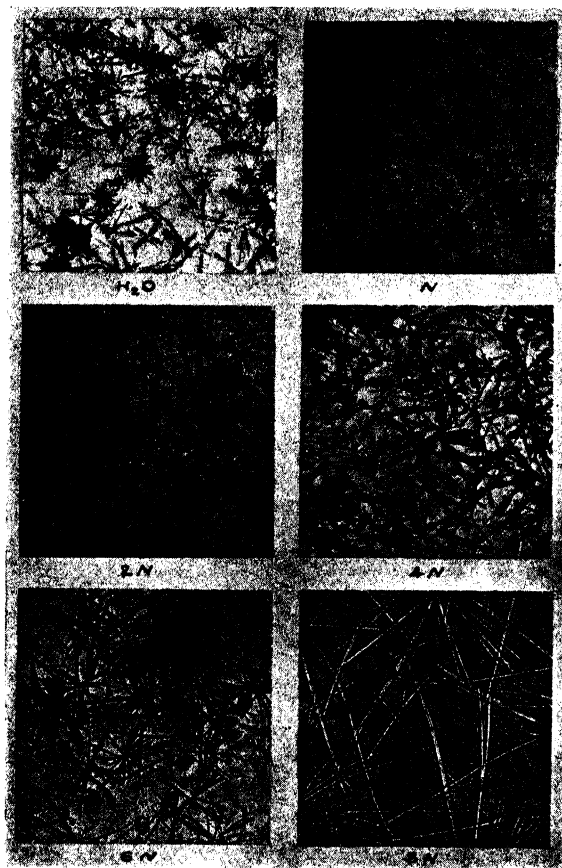
FIG. 13

Photomicrographs of Gypsum Crystals obtained in Various
Concentrations of NH_4CNS. ($\times$ 40)

TABLE VIII

Effect of $MgCl_2$ on the Setting of Plaster of Paris

Concentration of $MgCl_2$ solution normality	Time for maximum temperature	Solubility of gypsum from curve of Cameron and Seidell[1] Mols per liter
0.0	64.0	0.015
1.0	43.5	0.056
1.5	40.0	0.061
2.0	45.0	0.063
3.0	53.5	0.063
4.0	72.0	0.054
5.0	180.0	0.035

[1] J. Phys. Chem., **5**, 643 (1901).

Effect of Sodium Chloride. The effect of sodium chloride on the rate of set of plaster is similar in all essential respects to that of the ammonium salts as indicated by the data recorded in Table VII and plotted in Fig. 12.

Effect of Magnesium Chloride. Observations of the time required to reach the maximum temperature when varying concentrations of magnesium chloride solution are mixed with plaster of Paris are given in Table VIII and plotted with the other curves in Fig. 12. It is obvious that the general form of the curve is the same irrespective of whether a salt of a divalent or of a univalent cation is employed.

Effect of Ammonium Acetate. Certain organic salts such as ammonium acetate and ammonium citrate have been called retarders since they were found to slow down the rate of set of plaster of Paris even when present in low concentrations. This observation was confirmed with ammonium acetate as shown by the data recorded in Table IX from which the curve in Fig. 12 was obtained.

TABLE IX

Effect of $NH_4C_2H_3O_2$ on the Setting of Plaster of Paris

Concentration of $NH_4C_2H_3O_2$ solution normality	Time for maximum temperature	Solubility of gypsum estimated from data by Cohn[1] Mol per liter	Tensile strength pounds/sq.in.	
			after 1 day	after 10 days
0.0	64	—	235	490
0.04	64	—	——	——
0.10	83	0.06	100	240
0.50	240	0.15	125	250

The reason for the marked retarding action of $NH_4C_2H_3O_2$ solution in concentrations as low as $N/10$ and for the extremely low rate of reaction in $N/2$ solution calls for special consideration.

On several occasions[2] attention has been called to the fact that the rate of formation of a precipitate and the nature of the precipitate is not regulated generally and uniformly by its solubility and the supersaturation prevailing in accord with the theory of von Weimarn. The latter has taken care of variations from his theory by the introduction into his equations of what he calls "variable multipliers" the value for any substance being "the product of all other factors (in addition to P/L) which influence the crystallization process." This statement of von Weimarn is a frank admission that factors other than solubility do come in; but his formulation is of no help in solving the problem as to what factor or factors other than the solubility of hemihydrate and gypsum in ammonium acetate accounts for the apparently abnormal behavior of the plaster in contact even with low concentrations of the solution.

[1] J. prakt. Chem., (2) **35**, 43 (1887).

[2] Weiser and Bloxsom: J. Phys. Chem., **28**, 26 (1924); Weiser and Cunningham: **33**, 301 (1929); Weiser: "The Colloidal Salts", 1 (1928).

Photomicrographs of the crystals of gypsum obtained in dilute ammonium acetate solutions are reproduced in Fig. 14. It will be noted that the crystals are quite different in appearance from the needle-like crystals usually obtained. Those grown in the $N/10$ solution are short thick crystals while those grown in the $N/2$ solution consist of very thin hexagonal plates. This difference in appearance suggested the possibility that the abnormal behavior in acetate solutions might be due to a difference in the crystal structure of the gypsum formed.
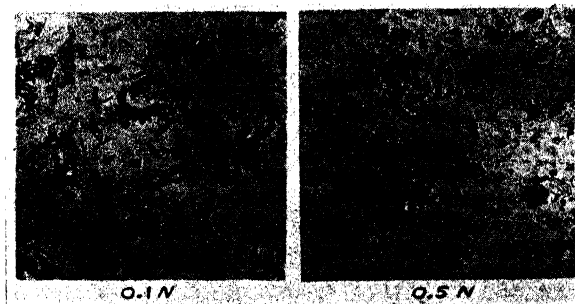
FIG. 14

Photomicrographs of Gypsum Crystals obtained in 0.1 Normal and 0.5 Normal Ammonium Acetate ($\times$ 40).

X-ray Analysis of Gypsum

To determine whether the gypsum formed in acetate solution possessed the same structure as that obtained in pure water the x-ray diffraction patterns of different samples were made with the General Electric X-ray Diffraction Apparatus. At the same time the crystals from other solutions were subjected to x-ray analysis to determine whether or not they were chiefly gypsum. Thus the crystals formed in strong solutions of NH_4NO_3 and $(NH_4)_2SO_4$ were so different in appearance from the usual small needle crystals that it was not certain but that the precipitates were double or complex salts. The crystals for analysis were prepared by mixing plaster and solutions in the same ratio as was used in preparing the slides for optical observations. The mixture was spread out thinly in a crystallizing dish and placed in a covered vessel containing water to prevent evaporation. After the reaction was complete (in the case of the $N/2$ $NH_4C_2H_3O_2$, after 2 days) the crystals were washed, dried, placed in a small capillary tube and the x-radiograms prepared by 8 hours' exposure. In Fig. 15 are reproduced photographs of the diffraction patterns for (1) plaster of Paris; and of the products formed by the action of plaster with (2) water, after 1 month (3) water, after 1 hour (4) 0.5 N $NH_4C_2H_3O_2$ (5) 10 N NH_4NO_3 (6) 7 N $(NH_4)_2SO_4$. It will be seen that the diffraction patterns of all the samples, except that of plaster of Paris, are identical. This indicates the instability of the alleged rhombic form of gypsum[1] and shows that the presence of electrolytes during the precipitation does not modify appreciably their composition or structure.

[1] Cf. Davis: J. Soc. Chem. Ind., **26**, 727 (1907).
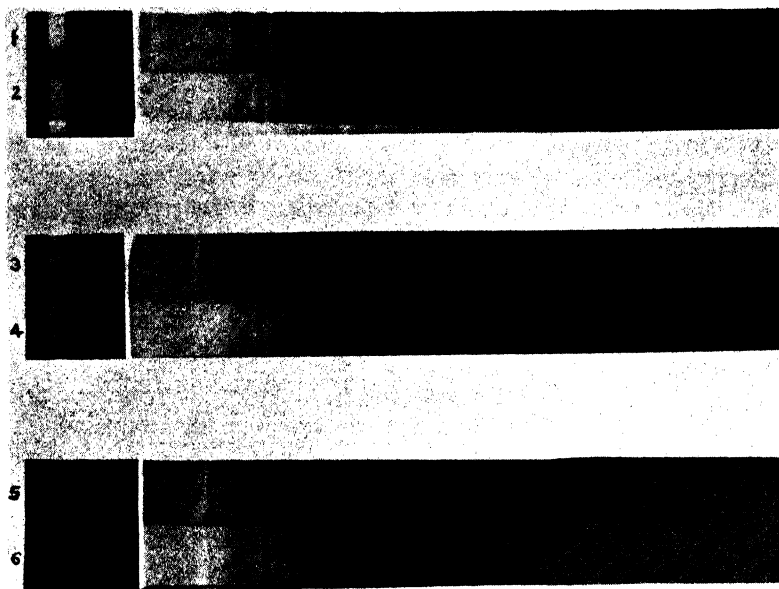
FIG. 15

X-Ray Diffraction Patterns of (1) Plaster of Paris and of the Products formed by the Action of Plaster with (2) H_2O after 1 month (3) H_2O after 1 hour (4) 0.5 N $NH_4C_2H_3O_2$ (5) 10 N NH_4NO_3 (6) 7 N $(NH_4)_2SO_4$.

Effect of adding Gypsum Nuclei to Plaster of Paris on the Rate of Set in Solutions of Foreign Electrolytes

Since the slowness of set of plaster in dilute ammonium acetate solutions is not due to the formation of a gypsum of different crystal structure, an attempt was made to determine whether the retarding was due primarily to the slowness of formation of nuclei or to the failure to precipitate even in the presence of nuclei. Hansen's observations with $N/10$ $NH_4C_2H_3O_2$ indicate that the first factor is important since he found that the time for attaining the maximum temperature was decreased from approximately 85 minutes to 55 minutes by shaking the acetate solutions for 35 minutes with a few grams of plaster of Paris before mixing it with the bulk of the sample. This increase in rate is not as large as one might expect from the observed effect of nuclei in the absence of electrolytes as shown in Fig. 2 of this paper. This could be due either to the formation of relatively few gypsum nuclei by only 35 minutes' action of $N/10$ acetate solution or to relative slow growth on the nuclei. To determine, if possible, what is the effect of added nuclei, the time-temperature curves were obtained for pastes prepared by mixing 35 cc of $N/10$ $NH_4C_2H_3O_2$ with 50 grams of plaster to which was added (1) no gypsum (2) 0.5 gram of gypsum formed by the action of water on hemihydrate, dried and ground and (3) 0.5 gram of gypsum formed by the action of $N/10$ ammonium acetate solution on hemihydrate, washed, dried, and ground (4) same as 3 except that the gypsum

sample was not washed, dried, or ground. The latter sample was prepared by adding plaster to the acetate solution and stirring gently with a current of air for several hours. The dried gypsum which passed a 100-mesh sieve was mixed thoroughly with the plaster before adding the electrolyte while the moist gypsum was suspended in the electrolyte before mixing with the plaster. The observations were repeated using $N/2$ $NH_4C_2H_3O_2$ instead of the $N/10$ solution. The results are summarized in Table X. The time-temperature curves for the various seeded samples with $N/2$ $NH_4C_2H_3O_2$ are reproduced in Fig. 16.

TABLE X

Effect of Seeding with Gypsum on the Rate of Set of Plaster of Paris—— Electrolyte Mixtures

Electrolyte added 35 cc	50 g Plaster of Paris seeded with	Time for maximum temperature
0.1 N $NH_4C_2H_3O_2$	0	83
0.1 N ″	0.5 g gypsum formed in H_2O, dried, and ground	19
0.1 N ″	0.5 g gypsum formed in 0.1 N $NH_4C_2H_3O_2$, washed, dried and ground	19
0.1 N ″	0.5 g gypsum formed in 0.1 N $NH_4C_2H_3O_2$ not washed, dried and ground	68
0.5 N $NH_4C_2H_3O_2$	0	240
0.5 N ″	0.5 g gypsum formed in H_2O, dried and ground	43
0.5 N ″	0.5 g gypsum formed in 0.5 N $NH_4C_2H_3O_2$, washed, dried and ground	55
0.5 N ″	0.5 g gypsum formed in 0.5 N $NH_4C_2H_3O_2$, not washed, dried and ground	206
10 N NH_4NO_3	0	121
10 N ″	0.5 g gypsum formed in H_2O, dried and ground	37

A reasonable explanation of the cause of the slowness of set of plaster in ammonium acetate solutions is furnished by these data. Comparing curve 1 with curve 4 of Fig. 16 it is evident that the addition of 1 percent of finely ground gypsum, formed in water, to plaster cuts down enormously the inhibition period, and decreases the time for reaching the maximum temperature from 240 minutes to 43 minutes. This means that the supersaturation is maintained sufficiently great that the growth on the added nuclei is fairly rapid. On the other hand, if the plaster is seeded by the same amount of the fine crystals formed in 0.5 N acetate and not washed, dried, and ground, the

rate is but little faster than if no nuclei at all are added (compare curves 3 and 4, Fig. 16). Evidently gypsum formed in the presence of acetate does not furnish satisfactory nuclei for starting the growth of the crystals; hence the precipitation from the supersaturated solution is greatly retarded. Since the crystal lattice is the same in gypsum formed in water as in gypsum formed in the acetate solution it is probable that the failure of the latter to act as effective nuclei is due to a film of acetate adsorbed on all the faces of the crystals. In support of this view it was found that washing, drying and grinding the
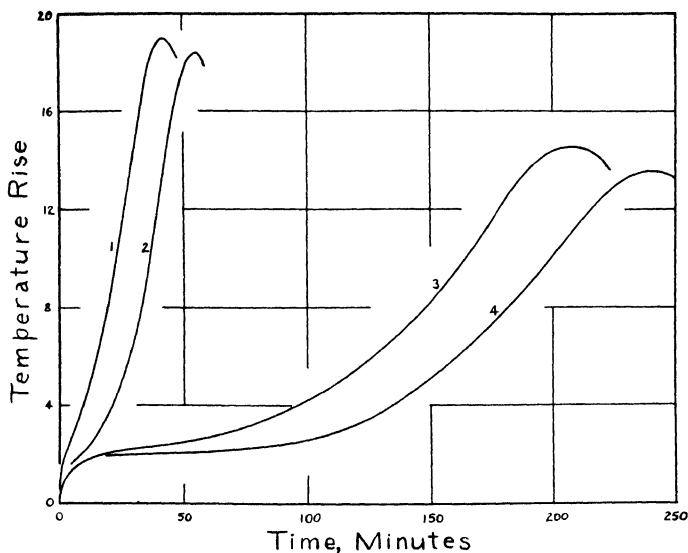
FIG. 16
Time-Temperature Curves obtained with Plaster of Paris in 0.5 N HN$_4$C$_2$H$_3$O$_2$ Solution Seeded with Gypsum Crystals formed in (1) H$_2$O (2) 0.5 N NH$_4$C$_2$H$_3$O$_2$ Solution, washed, dried, and ground (3) 0.5 N NH$_4$C$_2$H$_3$O$_2$ Solution not washed, dried, or ground (4) Not Seeded at all.

crystals formed in the presence of acetate gave effective nuclei and so accelerated the rate of set almost as greatly as the nuclei formed in water (compare curves 1 and 2 of Fig. 16).

The ultimate effect of ammonium acetate on the rate of set of plaster of Paris appears to be similar to that of small amounts of glue and gelatine, the adsorption of which on the gypsum nuclei inhibits or prevents the growth of the crystals and so delays or prevents the setting of the plaster.[1]

The addition of nuclei to the 10 N NH$_4$NO$_3$ plaster paste likewise speeds up the initial rate of reaction by cutting down the inhibition period and by furnishing a large number of centers of precipitation. (See Fig. 17.) Because of the low supersaturation, however, the reaction is slow in reaching completion even in the presence of added nuclei, as evidenced by the unusually broad portion in the region of maximum temperature in the time-temperature curve.

[1] Rohland: Z. anorg. Chem., 40, 182 (1904); Traube: Kolloid-Z., 25, 62 (1919); Ostwald and Wolski: 27, 78 (1920); Neville: J. Phys. Chem., 30, 1037 (1926).
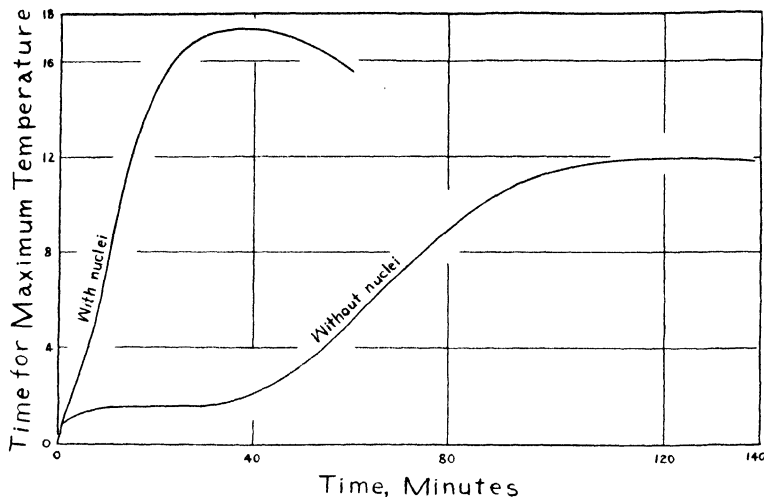
FIG. 17

Time-Temperatures Curves obtained with Plaster of Paris in 10 N NH$_4$NO$_3$ Solutions with and without the Addition of Gypsum Nuclei.

Summary and Conclusions

The results of these investigations are as follows:

1.   Thermometric and optical observations of the hydration of plaster of Paris were made with the end in view: (1) of throwing light on the existence or non-existence of gel formation as a stage in the setting process; and (2) of formulating a general theory of the effect of foreign electrolytes on the rate of set.

2.   A survey of the experimental evidence in support of the hypothesis that a jelly is formed before the interlacing mass of gypsum crystals is laid down, discloses the absence of any direct evidence of jelly formation. The indirect evidence is from two main sources: (1) the observation that gypsum can be thrown down under certain conditions as a gelatinous precipitate (Cavazzi, Neuberg) and as a jelly (Baykoff); and (2) the existence of a period of inhibition in the time-temperature curve which Neville attributes to the formation of a gel or adsorption complex between the plaster and water, a process accompanied by but little heat effect; and which Budnikoff attributes to the formation of a gel around the plaster particles protecting them from the action of water until crystallization of the gel takes place.

3.   Baykoff's gypsum jelly formed by shaking 10 percent (NH$_4$)$_2$SO$_4$ solution with an excess of plaster for 2 minutes and allowing to stand, is a "false gel" consisting of a mass of relatively large interlacing crystals of gypsum which have entangled water. The only point of resemblance between the cloudy, non-uniform, entangling mass of crystal needles and a silica jelly is that both stay in the containing vessel when the latter is inverted.

4.   The period of inhibition is not due to the formation of an adsorption complex between water and plaster "whereby the two reactants are brought

into chemical contact" (Neville); but is the result of delayed precipitation from a supersaturated solution owing to dearth of gypsum nuclei. The period of inhibition can be completely eliminated by the addition of less than 1 percent of finely powdered gypsum to the plaster.

5. When the time to attain the maximum temperature is plotted against the weight of finely powdered gypsum added to the plaster, a parabolic curve is obtained. By using the equation for this curve the initial amount of gypsum nuclei in a slow-setting plaster can be calculated. A sample containing less than 0.1 milligram of gypsum in 50 grams required 100 minutes to attain the maximum temperature on mixing with 35 grams of water while a sample containing 0.5 gram of gypsum in 50 grams attained the maximum temperature in 14 minutes. The tensile strength of the two samples of set plaster was approximately the same.

6. Suitable ignition to eliminate gypsum nuclei is all that is necessary to obtain a relatively slow setting plaster of Paris and the rate of set can be increased to any desired point by seeding with a suitable amount of finely powdered gypsum.

7. Rapid stirring of a plaster of Paris-water mixture increases the rate of set by breaking down the supersaturated solution of gypsum supplying nuclei and thereby decreasing the length of the induction period. When time of stirring is plotted against time for attaining the maximum temperature, a parabolic curve results similar to that obtained by the direct addition of varying amounts of gypsum to the plaster. (See 5 above.)

8. Since the setting of plaster of Paris involves the precipitation of gypsum from its supersaturated solution (Lavoisier, LeChatelier) the effect of foreign electrolytes on the process may be considered in the light of von Weimarn's theory of the rate of precipitation of nuclei and of the Nernst-Noyes equation for the rate of growth on nuclei as a result of diffusion. In general, the initial rate of formation of nuclei is proportional to $(Q-L)/L$ where Q is the total concentration of the substance which is to precipitate and L the solubility. $(Q-L)/L = P/L$ is the percentage supersaturation. The velocity of growth on the crystal nuclei, under otherwise constant conditions, is determined by $Q - L$, the absolute supersaturation.

9. The ratio of the solubility of plaster of Paris to that of gypsum in water at 25° is 4.5. If the saturation concentration of plaster of Paris hydrates to gypsum without precipitation, the percentage supersaturation is 3.5. Because of the relatively long inhibition period with pure plaster, this percentage supersaturation is insufficient to cause rapid initial precipitation of nuclei which must be present for a rapid reaction to take place throughout the mass of the plaster.

10. If the addition of a foreign electrolyte to water cuts down the period of inhibition, it follows in accord with von Weimarn's theory that the initial percentage supersaturation of the solution with respect to gypsum must be definitely increased. This may be accomplished in one of two ways: either the solubility of the hemihydrate is increased appreciably more than that of

gypsum in the presence of the foreign electrolyte or the solubility of the gypsum is decreased appreciably more than that of hemihydrate by the presence of the foreign electrolyte. In the first case P/L is increased because $Q - L = P$ is increased proportionately more than L; and in the second case P/L is increased because L is decreased proportionately more than P. Conversely, if the addition of a foreign electrolyte to water lengthens the inhibition period the initial percentage supersaturation of the solution with respect to gypsum should be decreased.

11. In general, for a foreign electrolyte to change the initial rate of formation of nuclei and hence the rate of set as compared to the rate in water alone, all that is necessary, other things being equal, is for the ratio of the solubility of hemihydrate to the solubility of gypsum to be greater or less than 4.5, the ratio of the solubilities in pure water.

12. The form of the gypsum crystals in the set plaster is influenced in great measure by the factors determining the absolute supersaturation and the number of nuclei. If L is small so that the $Q - L$ value is relatively large, the crystals grow very rapidly and are not well formed; while if L is large so that $Q - L$ is relatively small, large well-formed crystals result, provided the plaster is not seeded with gypsum nuclei.

13. The above deductions have been confirmed by extended thermometric and microscopic observations on the setting of plaster of Paris in solutions of varying concentrations of NH_4NO_3, NH_4Cl, NH_4CNS, $(NH_4)_2SO_4$, $NaCl$ and $MgCl_2$.

14. Contrary to what would be predicted from von Weimarn's theory the rate of set of plaster of Paris in dilute $NH_4C_2H_3O_2$ solutions is much slower than would be expected from solubility relations and the prevailing supersaturation. The reason for the retarding action of $NH_4C_2H_3O_2$ is that gypsum does not deposit readily from its supersaturated solution on gypsum nuclei formed in the presence of $NH_4C_2H_3O_2$ probably because of an adsorbed film of acetate on all the surfaces of the crystals. The addition of gypsum nuclei formed in the absence of acetate, induce a rapid rate of set.

15. The effect of such salts as ammonium acetate and ammonium citrate on the rate of set of plaster of Paris is similar to that of small amounts of glue and gelatin, the adsorption of which on the gypsum nuclei inhibits or prevents the growth of the crystals and so delays or prevents the setting of the plaster.

16. X-radiograms of the widely different forms of crystals obtained by the actions of plaster in solutions of the several electrolytes, disclose that the crystals are identical in structure with gypsum formed in the presence of H_2O alone.

The Rice Institute,
Houston, Texas.

THE KELLY TUBE AND THE SEDIMENTATION
OF PORTLAND CEMENT

BY CHARLES G. DUNCOMBE AND JAMES R. WITHROW

Introduction

This paper, after reporting the results of work done on the sedimentation of cement samples, using Kelly's sedimentation tube, describes a newly developed apparatus used in obtaining rates of settling of portland cement.

It is well known that there are a large number of pulverized products or fine powders in commercial production at the present time and that the degree of fineness is of great interest to many manufacturers and consumers of materials. Cements, pigments, and rubber fillers are a few examples of such materials. It is almost as well known that there is no method for the determination of fineness available for use in control laboratories with complete satisfaction. The control laboratory desires a method which may be carried out by the average laboratory worker with but little preliminary training and, in addition, that the method be carried out without the use of expensive or complicated apparatus. Finally, the method should permit the evaluation of fineness in at least two hours from the time that the sample is received from the grinding department or the receiving platform, as the case may be.

The well known and easily operated screening test meets the requirements of the control laboratory in these respects but cannot be used successfully for sizes much smaller than 200 mesh because of variations in size of wire and mesh and because of difficulties in obtaining peptization or preventing agglomeration.

Disregarding requirements of the control laboratory, there are several methods for the determination of the fineness of powders which have been largely developed in the field of colloid chemistry. In general these methods are (1) microscopic measuring and counting, (2) elutriation followed by microscopic measuring and counting, and (3) sedimentation methods.

This paper describes work done on one form of sedimentation method, using cement as the powder to be studied. We have worked on cement because of interest in cement production problems. Sedimentation analysis was selected for investigation because it was felt that this group of methods offered opportunities for the development of a control method. From the group of methods based on separation followed by microscopic measuring and counting, the air analyzer has already developed into a tool in use to some extent in control laboratories. This analyzer, developed by Pearson and

Sligh[1] will, according to Gonnerman[2] produce a single separation in from 60 to 100 minutes and, by repeating the separations with changes in the apparatus or conditions, as many separations as desired to show the fineness distribution may be obtained.

The microscopic methods have been reviewed by Work.[3] It does not seem likely that the use of the microscope will ever be popular in control laboratories for determining fineness since such use would involve not only the possession of a microscope but also the employment of a worker skilled in its use.

Literature

A review of sedimentation methods and a mathematical analysis of these methods has been contributed by Odén.[4]

The sedimentation methods based on a study of uniform suspensions can, according to Odén, be subjected to mathematical analysis under one of the following heads:

1. The variation of the specific gravity and the concentration with time at a definite distance below the surface of the suspension.

2. The variation of the specific gravity and the concentration with distance from the surface at a definite time.

3. The variation of the hydrostatic pressure with the time at a definite distance from the surface.

4. The variation in weight on an immersed body with time.

5. The variation in hydrostatic pressure with distance from the surface at a definite time.

6. Accumulation of the particles on the bottom as a function of time.

Odén also describes methods of Audubach and of Werner where uniform suspensions were not used but the dispersed sample was placed at the top of a column of fluid and the rate of settling observed. References to further use of these methods could not be found in the literature and it appears that they have not come into established use.

With the exception of the methods of Audubach and Werner, all of the methods of sedimentation analysis described by Odén depend on studying the rate of change of some property of a uniform suspension either with respect to time or with respect to distance from the surface after a definite time has elapsed. Special methods of treatment of the observed data are necessary in order to obtain the particle size distribution of the sample. It is not the purpose of this paper to discuss or consider these special methods of treatment and references regarding them are, therefore, not made.

[1] J. C. Pearson and W. H. Sligh. An Air Analyzer for determining the Fineness of Cement. Technical Paper No. 48. U. S. Bureau of Standards, Washington, D. C., September 8th, 1915.

[2] H. F. Gonnerman, Manager of Laboratory, Portland Cement Association. Private Communication to James R. Withrow, July 10th, 1929.

[3] Lincoln T. Work. "The Graphical Analysis of Distribution Curves for Pulverized Materials." Ph.D. Dissertation, Columbia University, New York City, (1928).

[4] Jerome Alexander: "Colloid Chemistry," pp. 861 et seq. (1926).

After some examination of the literature, it appeared that the methods of the third group were the simplest and required less apparatus than any other group, with the possible exception of the hydrometer method. Accordingly, attention was concentrated on the literature of the third group, namely the variation of the hydrostatic pressure with time at a definite distance from the surface of the suspension.

Wiegner's apparatus, which was the first to be described in which the rate of change of the hydrostatic head at a certain distance below the level of the suspension was measured with respect to time, consisted of a tube similar to that shown in Fig. 1. Ostwald and von Hahn modified this tube by placing the stop cock at the top of the tube of small diameter, hereafter referred to as
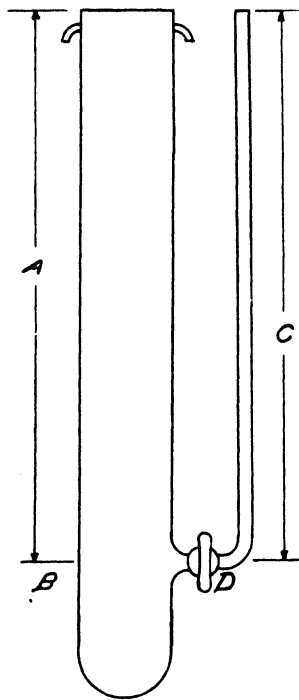
FIG. 1
Wiegner's Sedimentation Tube
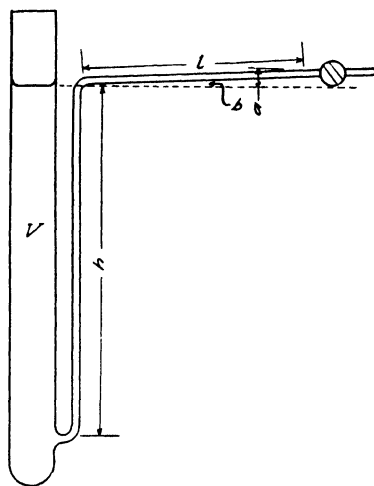
FIG. 2
Kelly's Original Sedimentation Tube

the side tube. Gessner and Wiegner mounted a light source in front of the side tube and a camera, containing a sensitized paper mounted on a moving drum, behind the side tube and obtained a photographic image showing the fall curve directly. All of these workers employed relatively concentrated suspensions, often containing as much as 50 grams per liter of the solid. Lorenz, who employed essentially the photographic apparatus of Gessner, recommended a concentration of from 2–4%.

Kelly[1] recognized that the use of concentrated suspensions was not desirable and described an apparatus, which he developed so as to permit the use of more dilute suspensions. Kelly's original tube is shown in Fig. 2.

[1] Ind. Eng. Chem., **16**, 928 (1924); Colloid Symposium Monograph, **2**, 29 (1925).

As a result of experimental work, he found that the rate of evaporation from the side tube which he used was a source of error and he proposed a modified form of the tube which is shown in Fig. 3. This tube, according to Kelly, had not been built when his article was written.

That class of sedimentation method in which the variation in hydrostatic pressure at a fixed point below the level of the suspension is observed as settling proceeds, appeared to be worth further investigation as the source of a method which might be suitable for control purposes. Of the apparatus of this type, the tube of Kelly appeared at first sight to be sufficiently simple and to possess advantages over other tubes of this class. Consequently, it was decided to utilize this tube for the first stages of the work which was to carry out sedimentation of cement samples, to make a study of the accuracy and convenience of the method, and to improve the accuracy and convenience wherever possible or desirable.

I. Experimental Work with the Kelly Tube

The Kelly Equation. Kelly derived a formula for use with his tube and in the derivation the assumption is made that the height of the suspension remains constant throughout a sedimentation.

FIG. 3
Kelly's Proposed Sedimentation Tube

It appears that this may not be strictly true and that error may be introduced by this assumption. Accordingly the formula was, first of all, subjected to critical examination.

Kelly developed his formula by setting the hydrostatic pressure of the suspension equal to the hydrostatic pressure of the clear liquid in the side tube at the junction of the side tube to the main tube which contains the suspension. Thus, referring to Fig. 2,

$$D h = d (a+h) \tag{1}$$

where D is the density of the suspension and d is the density of the clear liquid in the side tube (and also the suspending liquid). D is equal to

$$\frac{(V-v)d + w}{V} \tag{2}$$

where V is the volume of the suspension above the entrance to the side tube and v is the volume of the pigment in suspension whose weight is w. Also

$$a = l \sin b \tag{3}$$

where b is the angle which the horizontal portion of the side tube makes with the exact horizontal. Substituting equations (2) and (3) in equation (1) and

transposing, Kelly arrives at the following expression for the weight in suspension:

$$w = \frac{dVS\ l\ \sin b}{h\ (S-d)} \tag{4}$$

where S is the specific gravity of the pigment in suspension. According to Kelly, since w and l are the only variables for a given experiment, equation (4) reduces to the form

$$w = K\ l \tag{4a}$$

in which form it is conveniently used.

Although Kelly did not go into this, for evaluation of the distribution of fineness it is convenient to obtain the weight settled. Kelly's formula (4) is easily extended to this form by remembering that the weight settled equals the weight in suspension at the start minus the weight in suspension at the time in question, or

$$\text{weight settled} = \frac{dVS\ \sin b\ (l_o - l_t)}{h(S-d)} \tag{5}$$

where l_o is the reading at zero time and l_t is the reading of the manometer side tube at the time in question.

The formula of Kelly is developed under the assumption that "h," the height of the suspension remains constant. It does not appear that this is strictly true for, as the solid settles out, the meniscus in the side tube recedes and, in so doing, transfers a quantity of liquid to the main tube, thus increasing the height of the suspension. For one centimeter of travel by the meniscus there will be a definite increase in the height of the suspension depending first on the volume of liquid in the side tube per centimeter of length and second on the centimeters of height of liquid in the main tube per cubic centimeter. The product of these two values is the increase in height in the vertical tube for one centimeter of travel of the meniscus along the side tube.

Thus, in Kelly's original equation (1), the term "h" should be replaced by the term "h $+ \triangle$h," where "h" is the height of the suspension at the start of the experiment. Accordingly, we have

$$D(h + \triangle h) = (a + h)\ d \tag{6}$$

Repeating the development as before and neglecting the effect of the liquid flowing into the vertical tube from the side tube on the density of the suspension, we obtain for the weight in suspension

$$w = \frac{(l\ \sin b - \triangle h)\ d\ VS}{h(S-d)} \tag{7}$$

Representing the increase in height in the vertical tube caused by the recession of the meniscus over a distance of one centimeter by the term C_1 is permissible, since, for a given tube, this is constant. Also the term "sin b" may be represented by C_2 since it is also constant for a given tube. Thus we obtain (for the weight settled)

$$w = \frac{dVS\ (l_o - l_t)\ (C_1 + C_2)}{h(S - D)} \tag{8}$$

or
$$w = K''(l_o - l_t) \tag{9}$$

Effect of Tube Dimensions on Equation Error. The amount of error which is introduced by assuming h to be constant may be calculated by assuming that formula (8) is correct. Comparing this with equation (5), the error is proportional to the term C_1 and the percent error is given by the expression

$$\frac{C_1}{C_1 + C_2} \times 100 \tag{10}$$

In the tube suggested by Kelly in which he recommended an angle of inclination of $1°30'$ and a bore of 2 mm. for the side tube and a diameter of 2 cms. for the vertical tube, C_1 takes the value of 0.01 and C_2 the value of 0.0262 from which the percent error would be 28 percent.

With the Kelly tube used in this work, to be described later, the sine of the angle or C_2 was 0.02. The diameter of the side tube was 2.5 mm. and 135.5 ccs. were contained in 34 cms. of height in the vertical tube. C_1 was thus 0.012 from which the percent error was $37\frac{1}{2}$ percent.

In a tube constructed according to the idea of Kelly, described by Mack and France[1] 2.38 centimeters of horizontal side tube contained 0.1 cc. and 25.2 centimeters of height in the vertical tube contained 99 ccs. Thus C_1 was 0.01. C_2 was given as 0.03. Therefore, in this tube the error in weight settled amounts to 25 percent.[2]

For solids which settle out completely and a reading thus obtained for the completely settled condition, the final reading may be designated by l_∞ and the total weight settled becomes, from equation (8)

$$w_\infty = \frac{dVS\ (l_o - l_\infty)}{h(S - d)}\ (C_1 + C_2) \tag{11}$$

Since percent settled at any time is the ratio of the weight settled at that time compared to the total weight settled and multiplied by 100, or in the ratio of equation (8) to equation (11) all of the constants vanish and the expression reduces to the form

$$\frac{l_o - l_t}{l_o - l_\infty} \times 100 \tag{12}$$

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[1] "A Laboratory Manual of Elementary Physical Chemistry," 182 (1928).

[2] During discussion of the paper, R. Bradfield questioned the validity of all sedimentation methods because Keen and Crowther have shown that, in the case of the Kelly tube, when the clear liquid enters the main tube from the side tube, it does not displace the suspension upward but travels up the side of the tube and, in so doing, sets up eddy currents and that these eddy currents introduce errors which are much larger than that caused by neglecting the increase in height of the suspension in determining the weight of solid in suspension or settled out. This objection may have some weight in the case of the Kelly tube. We have no experimental data on it. However, the modified apparatus described later in the paper, transferred only about 0.0012 cc. of liquid from the side tube to the main tube over a period of several days. It would appear that such eddy currents, if produced at all, must be very slight and of small effect, in this case.

From this it is evident that, if percent settled is calculated directly from the readings, using equation (12), all constants of the Kelly formula vanish and they need not be determined at all. In addition, one step of the calculation is eliminated, since the results must be calculated to percent settled in any event, in order to be susceptible to the special treatment by which distribution data is obtained.

However, for another purpose, the evaluation of the Stokes equation, it is necessary to determine the density and viscosity of the liquid and the density of the solid as well as the height of the suspension above the entrance to the side tube.

Apparatus. The first sedimentation tubes constructed for use in this work were similar to that illustrated in Fig. 3. However, the small bulbs located at the outer end of the side tube were a source of trouble. They rendered the tubes more difficult to clean and dry and, when the bulbs were charged with liquid preliminary to starting a run, careful handling was required to prevent transferring some of the liquid to a portion of the capillary directly adjacent to the bulb where a short column or meniscus of the liquid would be formed. After liquid had been placed in the bulb, the side tube had to be filled with clear liquid and then excess of clear liquid poured out of the vertical tube and here accidents were frequent. Finally, the extremely rapid reaction of settling required considerable speed in starting and prevented careful and fine adjustment of the level of the suspension and, as a result of this, often the level would be too high, forcing the side tube liquid into the bulb and requiring complete emptying and restarting of the run. Consequently, the bulbs were eliminated from this position. Experimental work showed that some form of bulb was absolutely necessary and therefore the bulbs were constructed separately and mounted on the end of the side tube by means of glass tubing and mercury seals. The protection bulb finally used for the large tube was also separately constructed and was attached by means of a cork covered on the inside with tin foil and sodium silicate. The most satisfactory scale was obtained by lashing a thermometer to the horizontal portion of the side tube. Fig. 4 shows the complete tube used in the latter runs. Two of these improved tubes were constructed, whose dimensions are given in Table I.
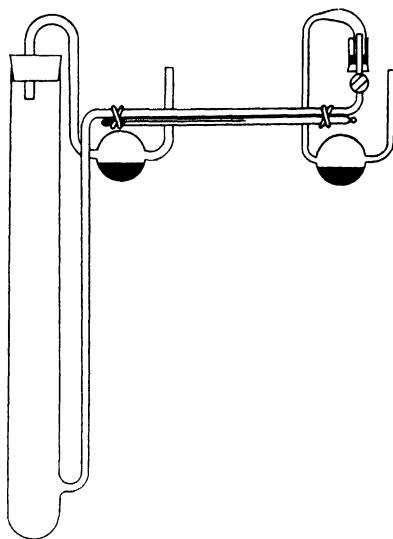
Fig. 4
Modified Form of Kelly Tube

TABLE I

Dimensions of Kelly Sedimentation Tubes

	Tube 1	Tube 2
Total height, vertical tube	47 cms.	47 cms.
Inside diameter, vertical tube	23 mm.	23 mm.
Inside diameter, manometer tube	2.5 mm.	2.5 mm.
Length of scale, manometer tube	35 cms.	34 cms.
Height of manometer scale above side tube connection	34 cms.	32 cms.
Height of side tube connection above bottom of large tube	6 cms.	5.5 cms.

Procedure. In the first experiments, efforts were made to use a definite weight of sample with a view to obtaining some confirmation of the improved formula already developed (equation 8). This involved the preparation of a suspension having less volume than actually required and complete transfer of this suspension to the tube with subsequent addition of sufficient clear liquid to adjust the level to the desired place. This, in turn, required mixing the suspension in the tube before starting a run. After several experiments, this procedure was abandoned and an excess of suspension was prepared from which the tube was filled as rapidly as possible.

In the selection of the details of the procedure, it is to be recognized that cement is a material which cannot be subjected to sedimentation analysis in water or an aqueous solution because the action of the water on the cement would alter the condition of the particles under investigation. Even the use of substances in which water is an impurity such as glycerin, alcohol, etc., can only be used after an investigation shows that cement cannot remove water from such materials. Mineral oil, after refining, is probably less liable to contain water than the majority of liquids. Therefore we arbitrarily elected to use stanolind, a water-white refined mineral oil of high viscosity, and to mix this with kerosene in proportions to produce a liquid mixture of the desired viscosity.

It was found that when a high viscosity liquid, produced by using 65 percent stanolind and 35 percent kerosene, was used in the side tube, approximately 20 minutes was required for the meniscus to come to equilibrium after a small disturbance. This lag is fatal to sedimentation and shows that a liquid of low viscosity must be used in the side tube. Theoretical considerations show that a combination of two liquids of different viscosity and density one in the side tube and the other in the vertical tube can be used without complicating the calculations or invalidating the results, if the readings are calculated directly to percent settled. There must be no interchange of the two liquids in the side tube although the flow of the manometer tube liquid into the vertical tube does no harm, except possibly to create eddy currents. Toluol was selected as the liquid to be used in the side tube.

Measurements showed that 134 ccs. were contained in each of the sedimentation tubes when filled to the proper level for starting. Arbitrarily, it was

decided to use 1.5 grams of cement in 150 cc. of oil, or a 1 percent suspension. It was found that, by heating the oil containing the sample, apparently good peptization was obtained. Since the character of the oil might conceivably change somewhat by this heating, viscosity and density measurements were made on samples of clear oil after each sedimentation had been completed.

Experiments showed that, when the wall of the vertical tube was wetted with the suspension above the level of the suspension during the course of filling, it required ten minutes for this liquid to drain down from the walls and as it drained down it increased the height of the suspension, thereby introducing an error which distorted the starting readings.

In the early runs, attempts were made to add the suspension to a definite mark on the vertical tube so located that, when the stop cock was opened, the meniscus in the side tube would arrive at a position near the outer end of the horizontal portion of the side tube. Experience showed that it was very difficult to do this, and in later runs, as soon as the stop cock was opened, a final rapid adjustment of the level of the suspension was made by means of a pipette. For the last few runs, in which protection bulbs were used over the large tubes, these bulbs were not affixed until the level had been adjusted.

As soon as the suspension had been added, a stop watch was started and readings of the position of the meniscus were thereafter taken with respect to time. Since it was impossible experimentally to obtain a zero reading, this was obtained by plotting the first few readings on an auxiliary curve and extrapolating back to zero time. The readings were calculated to percent settled as already indicated, namely, by taking the difference between the zero reading and the final reading as 100 percent settled and the difference between the zero reading and the reading at the time in question as proportional to the percent settled at that time.

Experimental Results. The experimental work covered a series of thirty runs. Of these the results of the last two runs were of most significance. The readings for these runs, quite similar to others, are shown in Table II, the readings for the early portions of the runs being omitted for the sake of brevity.

In neither of these runs did the readings ever become constant.

In other runs, however, the readings became constant after 20 or 21 days. In all of these runs, the liquid in the main tube appeared clear after approximately one week.

In several runs, the readings became constant while the suspension was still turbid, i.e., before settling was complete. In one, a tiny droplet of water was found in the side tube but in the others, no reason for the stationary meniscus could be found.

In the early runs, entirely too many readings had to be ignored in drawing smooth curves, evidently due to fluctuations in the thermostat bath temperature, due to inadequate stirring. When the rate of stirring was increased, these variations were reduced.

The presence of lag was shown in preliminary experiments when a liquid of high viscosity (about 0.2 poise) was used in the side tube. This lag was

TABLE II

Rate of Settling, Cement Sample No. 2

Run 29		Run 30	
Time	Reading	Time	Reading
—	—	—	—
—	—	—	—
420 min.	82.4	315 min.	127.2
455	81.0	360	121.8
500	79.0	1135	115.0
19 hr. 15 min.	57.6	19 hr. 20 min.	113.5
22 15	55.4	21 35	112.4
24	53.6	23 25	111.8
25 45	51.8	25 35	111.0
28	50.5	41	105.5
43 25	45.5	49 25	103.7
52	43.7	70 15	100.3
72 40	40.2	113 20	95.0
115 45	36.0	122	94.0
124 15	34.9	140 10	92.8
142 35	33.6	8 days	89.7
8 days	29.3	12	86.2
12	24.0	15	83.9
15	20.1	19	83.0
19	17.0	20	82.5
20	15.8	22	81.5
22	13.0	24	79.5
24	11.4	26	78.0
26	10.0	28	77.0
28	8.0	31	76.0
31	5.5	35	74.5
35	2.0	40	72.2
40	−2.0	44	70.6
44	−5.0	48	67.9
48	−7.5	55	64.9
55	−11.0	57	64.0
		59	60.5

Readings stopped because meniscus went off scale. Side tube bulb still contained toluol.

After last reading, tube was removed No toluol was left in side tube bulb.

found to be approximately 20 minutes, i.e., when, after equilibrium had been obtained for the meniscus, the level was disturbed temporarily so as to displace the meniscus approximately 2 centimeters, it required approximately 20 minutes to return to nearly the same position or rather to a position of rest. The meniscus never did return to exactly the same position.

Several runs were deliberately extended only through the early stages of settling in order to study the conditions at the start of the run. Suspicion was aroused that a different shaped curve was obtained at the start of a run when the meniscus attained its position of dynamic equilibrium by a continuous and uninterrupted recession, than when it rose and then began to recede. These two types of start were the result of the method of adjusting the level of the suspension. Two runs were started with a falling meniscus, (uninterrupted recession) and two runs were started with arrested meniscus (first rising and then falling). When the readings were plotted in curve form, it was seen that, when the meniscus fell without interruption, the slope of the curve for the first ten minutes was steeper than when the meniscus has been arrested.

Five runs were regarded as completed runs when they were made and the percent settled was calculated. Table III shows some of the values from these runs.

TABLE III

Percent settled with Respect to Time

Time (min.)	Cement 1		Cement 2		
	Run 5	Run 6	Run 9	Run 15	Run 16
5	10.28	12.7	9.2	8.7	10.37
10	18.14	21.5	17.1	14.8	19.45
20	28.93	33.3	27.5	23.7	30.1
30	35.53	40.5	34.5	31.2	37.8
40	40.86	45.7	40.1	36.3	43.6
50	44.79	49.7	44.6	———	46.6
60	48.47	53.1	48.5		50.0

Runs 5 and 6 are directly comparable, being made in the same tube, at the same temperature, with the same height of suspension and using the same mixture of sedimentation oil. The three runs for cement 2 are only comparable within about 2 percent, since there was small differences in the height of the suspension between the three runs.

Discussion of Results. Run 29 and 30 showed that, even under the best conditions, using only glass and mercury seals and locating the bulbs of Kelly at approximately the same level as the liquid levels in the vertical tube and the side tube, respectively, evaporation continued to take place and a stationary position of the meniscus was never obtained. Other runs also showed this same behavior. This confirmed Kelly's observation on the run reported by him (a short one of approximately 8 hours) for, with longer runs than reported by Kelly, we find this error intensified.

Knowing that evaporation takes place, it is possible to explain the unusually long time required for a constant reading to be obtained in some of the runs. The fact that the meniscus ever became stationary in these runs must have been due to trouble such as was encountered in other runs where the meniscus became stationary before settling was complete.

It is apparent that the method used to obtain percent settled values depending, as it does, upon the obtaining of a final constant reading, cannot be directly used, if evaporation takes place. It is possible to prolong a run and perhaps obtain a constant rate of fall of the meniscus which would be due to evaporation alone and then to apply this evaporation correction to all readings taken. Such procedure would be entirely too laborious and time consuming to be of much value, if any other method can be made to serve.

Results of all runs made, therefore, whether initially regarded as successfully completed or not, must be regarded as affected with this evaporation error.

The percent settled values of the five runs cited cannot be considered as reliable because of evaporation loss. The fact that constant readings were ever obtained must have been due to some interfering substance or situation which caused the meniscus to become stationary. This could have happened at different relative times in the history of the runs and thereby affected the percent settled values. The evaporation loss did not affect the relative values of percent settled in the early history of the run and comparisons could be roughly made, except for the possibility of the meniscus having been arrested.

There is also the possibility that complete peptization was not obtained. There is no evidence to show that any of the samples were completely peptized. This does not, however, invalidate any of the results bearing on the operation or usefulness of the apparatus. Lack of peptization merely means larger particles.

In connection with the runs it is important to note that the method for calculating percent settled depends on extrapolation backwards to obtain a value for the reading at zero time. The total change in readings and therefore the value for 100 percent settled depends, in part, on the zero reading and, if this is incorrect, all percent settled values are in error as a result. To illustrate this, suppose that a total difference in readings of 150 was obtained but that the zero reading was 10 too low, in other words the correct difference in reading should be 160. Then at some intermediate reading, say for 50 percent apparently settled, the correct percent settled would be 85/160 instead of 75/150 or 53 percent. This is an error (3 percent in the example) which cannot be permitted to exist if it is possible to eliminate it.

In discussing the results, it should be stated that it was to be expected that troubles would be experienced traceable to the type of powder under examination. We are dealing with a powder which, from the screen analysis, is known to have about 10 percent residue on 200-mesh screen. It has been the object in this work to evaluate the coarse particles as well as the finer portion by sedimentation analysis.

In later work, to be described in another paper, it was found that the coarsest particles had a dimension of about 90 microns, equivalent radius, with the same sample of cement as was used in this work. When the density of the cement is taken as 3.295, the density of the oil as .86 and the viscosity of the oil as 0.18 poises and with a height of suspension of 77.7 cms., the time

corresponding to 90 microns is 5 minutes. This means that the first change in the rate of settling occurred in five minutes and the portion of the fall curve between zero and five minutes was a straight line. If the height of the suspension had been 30 centimeters (the approximate distance in this work) the time would have been approximately 2 minutes. The necessity of a viscous liquid is therefore obvious.

As already pointed out, such a viscous liquid cannot be used in the side tube because of lag, and toluol was used instead. Even with toluol, however, no straight portion of the fall curve was ever obtained. If the powder is finer, say all passing through 325 mesh screen, the situation is much different. Assuming a size of 20 microns equivalent radius for the largest particles and assuming other conditions as already noted, the time for 77.7 centimeters of fall becomes 100 minutes and for 30 centimeters of fall about 37 minutes. A less viscous liquid may then be used, the run shortened in time, no starting troubles met with, and the effect of the lag will be less in the side tube and a less volatile liquid can therefore be used in the side tube.

The results of the mathematical discussion which indicates that there is an error involved in the determination of weight in suspension by the use of the Kelly formula, has not been experimentally confirmed or even investigated in the work. It appears that there will only be a few cases where workers will have subjected themselves to this error since, as pointed out, it is easier to calculate the percent settled values directly from the readings.
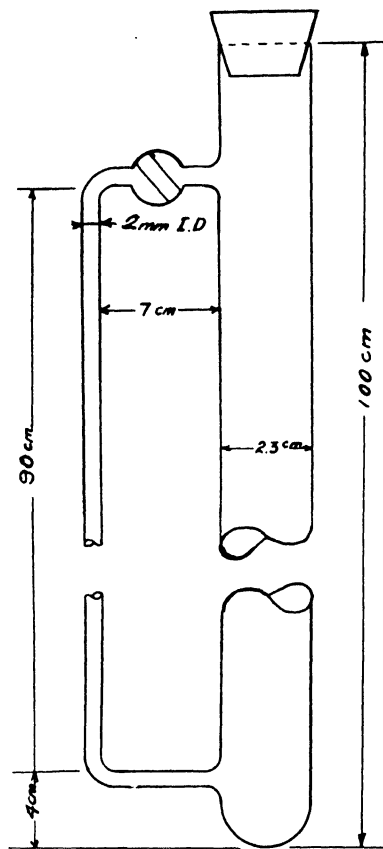
FIG. 5
Modified Form of Wiegner Tube

II. Experimental Work with Modified Wiegner Tube

Apparatus. Since the Kelly tube was not satisfactory for our work and we were loath to abandon the idea or general method, we examined the original apparatus of Wiegner. This tube (with the improvement of Ostwald and von Hahn), was successfully modified by us to provide an apparatus of extreme sensitivity by means of which successful sedimentations of cement were made.

Fig. 5 shows the details of the new glass sedimentation tube. The essential difference between this tube and the tube of Ostwald and von Hahn is that the side tube is bent over and re-enters the main tube at the top so as to provide a connection between the vapor space over the suspension and the vapor

space over the side tube liquid. This connection eliminates differences in vapor pressure due to slight differences in temperature and permits exposure of the vapor spaces to air of the room. Thus a cork, covered with tin foil, may be inserted in the top of the main tube and evaporation prevented.

The tube was suspended from the top by a sturdy clamp and this in turn was supported by a heavy metal pipe resting on concrete supports which were independent of the thermostat tank. The tube was immersed in a constant temperature bath 12″ x 12″ x 48″. The tank contained two windows, 6″ wide,
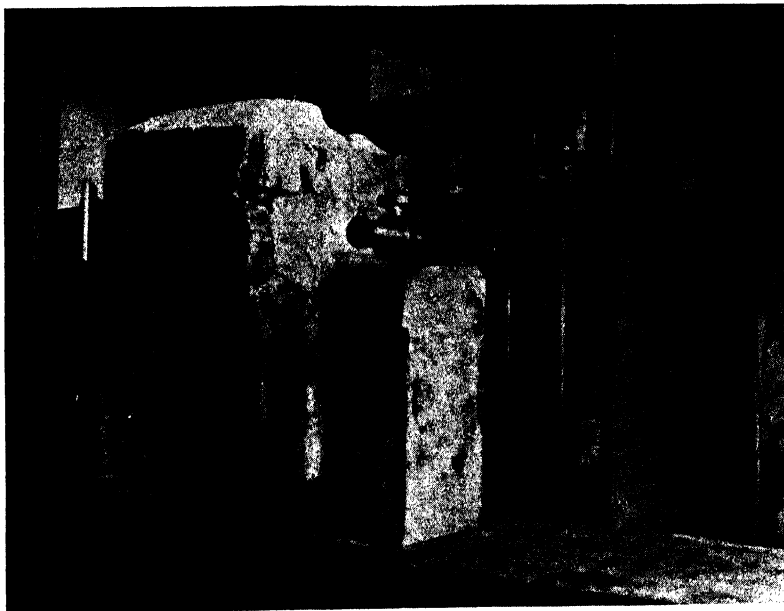
FIG. 6
View of Assembled Apparatus

extending the full height of the tank and placed on opposite sides. The sedimentation tube was placed so that the side tube was close to one window on the inside and a Gertner microscope with micrometer head, mounted on a horizontal support, was placed on the outside of the same window in such a position that the meniscus of the side tube was visible in the field of the microscope. A light was placed on the outside of the opposite window so as to illuminate the menisus. The assembled apparatus is shown in Fig. 6. Experience showed that the only difficult points about the construction and erection of the apparatus was the elimination of vibrations in the meniscus caused by stirring of the water and also the erection of the tube and microscope on firm supports.

Procedure. The suspensions were prepared in the same manner as previously outlined. Some of the clear liquid used in preparing the suspension was poured into the sedimentation tube and, by tilting, the side tube filled with clear liquid nearly up to the level at which the suspension would stand.

The stop cock was then closed and excess of liquid poured, after which the tube was placed in position. A large funnel was inserted in the top of the main tube and the suspension poured into the tube as rapidly as possible. A stop watch was then started, the cork inserted in the top of the main tube, the clamp of the tube loosened and the tube adjusted so that the meniscus came into the field of the microscope. The clamp was then tightened and readings were taken with respect to time by adjusting the cross hair of the micrometer eyepiece to the meniscus and observing the reading on the micrometer head.

In starting runs with this apparatus, two precautions were necessary. First the large funnel was used in order to prevent wetting the wall of the main tube above the level of the suspension and thereby introducing drainage error. Second, the upper side arm connection which contained the stop cock was kept entirely free of liquid, since if a drop of liquid was present, it found its way to the stop cock and stopped the vapor connection between the side tube and main tube.

A zero reading was obtained by extrapolation backwards. The final reading was taken when there was no change in the position of the meniscus over a period of two days. The microscope used had a scale range of approximately one-fifth of the complete change in level of the meniscus. Therefore, it was necessary to shift the position of the meniscus whenever it passed out of the field of the microscope. This was done by raising the tube. The tube could be shifted and the cross hair again brought to the meniscus within one minute. The last few readings taken before the shift and the first few readings taken after the shift were plotted and the two curves extended, the first one ahead and the second one back. Thus two readings were obtained for the same time value and the difference between the two readings represented the distance through which the tube had been raised, expressed in terms of micrometer head readings. It was only necessary to add this difference to all readings taken after the shift. When the second shift was made, the addition to be made consisted of two such differences.

In order to calculate the observed readings over to percent settled, the readings were tabulated in a continuous series which included the values for the shift of the tube. From these readings the value of the reading for zero time was subtracted which resulted in values of reading drop for the corresponding times. Using a slide rule, percent settled was calculated from reading drop by dividing the reading drop for the time in question by the total reading drop and multiplying the result by 100.

Data and Calculations. A preliminary test was made to determine the amount of evaporation loss. The side tube was filled with clear liquid and the tube adjusted to bring the meniscus into the field of the microscope. The cross hair was adjusted to the meniscus and the apparatus allowed to stand for five days with frequent observation. At all times the cross hair was found to be directly on the meniscus.

In order to determine the amount of the lag in the modified apparatus, the tube was filled with clear oil and the cross hair of the microscope brought to the meniscus. Approximately one-third cc. of oil was then added to the

large tube and the cross hair again brought to the meniscus as quickly as possible. It was found that approximately 200 divisions change were produced and that the position of the mensicus was constant after 20 seconds.

Preliminary observations showed that a change of one-half inch in the level of the water in the thermostat bath produced an observable change in the position of the meniscus.

It was found that there was an uncertainty in locating the position of the cross hair on the meniscus amounting to five divisions in either direction.
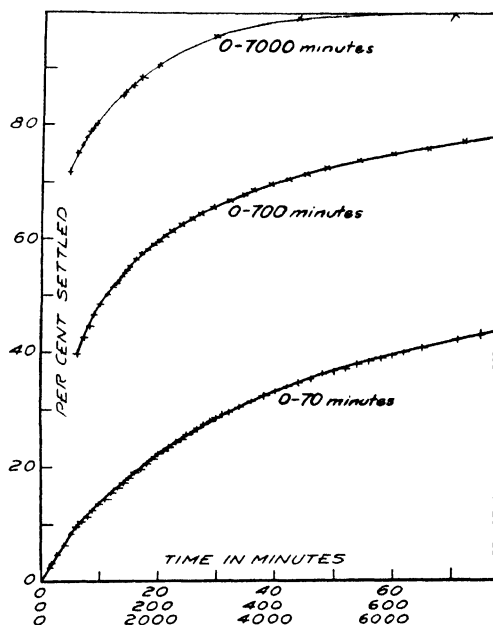
FIG. 7
Fall Curve Cement No. 2

Later work showed that as a rule the entire range through which the meniscus moved amounted to about 7500 divisions. Thus the measuring error was less than 0.1 percent.

It was observed that, when the temperature of the thermostat varied by more than 0.02 C., measured by a Beckmann thermometer, a variation in the position of the meniscus could be observed.

Fifteen sedimentation runs were made with this apparatus and twelve were successfully completed as far as the apparatus was concerned, *i. e.*, some of them were not considered as satisfactory because of lack of peptization or for other reasons not associated with the apparatus. Two runs were unsuccessful because of poor supports and one because of the presence of a drop of liquid in the stop cock of the upper side arm connection.

The data for one run are given in Table IV, and are also shown in curve form in Fig. 7.

TABLE IV

Sedimentation of Cement Sample 2, using newly Modified Tube

Weight of cement taken 3.0 grams. Dispersed in 300 cc. of sedimenting oil (65% stanolind 35% kerosene) by heating for 20 minutes and adding small piece of camphor. Dispersion stood in thermostat overnight with cover over jar. Temperature of thermostat 29° C. Density of cement 3.295. Density of oil (determined after sedimentation was complete) .8602. Viscosity of oil .1813 poises. Height of suspension 77.7 cms.

Reduced form of Stokes equation $r = (.000407/t)^{\frac{1}{2}}$
(for time in minutes)

Time (min.)	Reading	Reading drop	Percent settled
0	--25	000	00.00
1.5	148	173	2.26
2	211	236	3.08
3	331	356	4.65
4	452	477	6.22
5	594	619	8.08
6	688	713	9.29
7	765	790	10.30
8	846	871	11.34
9	931	956	12.47
10	1004	1029	13.40
11	1073	1098	14.31
12	1152	1177	15.34
13	1225	1250	16.30
14	1295	1320	17.20
15	1365	1390	18.11
16	1434	1459	19.00
17	1500	1525	19.87
18	1569	1594	20.80
19	1928	1653	21.55
20	1685	1710	22.30
21	1736	1761	22.97
22	1790	1815	23.65
23	1848	1868	24.35
24	1893	1918	25.00
25	1950	1975	25.75
26	1989	2014	26.22
27	2043	2068	26.97
28	2089	2114	27.55
29	2128	2153	28.05
30	2185	2210	28.85
31	2213	2238	29.20
32	2253	2278	29.70
34	2332	2357	30.72

TABLE IV (Continued)

Time (min.)	Reading	Reading drop	Percent settled
36	2404	2429	31.70
38	2464	2489	32.50
40	2532	2557	33.38
42	2587	2612	34.10
44	2650	2675	34.90
46	2714	2739	35.75
48	2771	2796	36.50
50	2812	2837	37.00
52	2853	2878	37.55
54	2904	2929	38.15
56	2947	2972	38.80
58	2987	3012	39.30
60	3028	3053	39.82
62	3073	3098	40.40
65	3129	3154	41.20
71	3243	3268	42.70
75	3314	3339	43.55
80	3404	3429	44.75
85	3486	3511	45.80
90	3558	3583	46.80
95	3625	3650	47.65
100	3694	3719	48.50
105	3754	3779	49.30
110	3818	3843	50.20
115	3873	3898	50.85
120	3924	3949	51.55
125	3977	4002	52.25
130	4023	4048	52.85
135	4069	4094	53.50
140	4121	4146	54.00
145	4165	4190	54.70
150	4207	4232	55.20
160	4297	4322	56.45
170	4377	4402	57.50
180	4445	4470	58.30
190	4508	4533	59.15
200	4568	4593	59.90
210	4626	4651	60.75
220	4683	4708	61.55
235	4758	4783	62.50
255	4845	4870	63.55
270	4911	4936	64.40
290	4992	5017	65.45
300	5033	5058	66.00

TABLE IV (Continued)

Time (min.)	Reading	Reading drop	Percent settled
320	5101	5126	66.90
345	5174	5199	67.80
360	5226	5251	68.60
390	5307	5332	69.60
420	5382	5407	70.60
450	5444	5469	71.40
485	5517	5542	72.75
540	5630	5655	73.90
600	5733	5758	75.02
660	5816	5841	76.25
720	5903	5928	77.40
780	5979	6004	78.90
840	6051	6076	79.30
900	6116	6141	80.10
1335	6493	6518	85.00
1400	6544	6569	85.75
1520	6639	6664	87.00
1680	6750	6775	88.50
1955	6899	6924	90.40
2925	7308	7323	95.50
4350	7552	7577	98.75
7020	7637	7662	100.00

Discussion of Results. The fact that the apparatus stood for five days without any observable change in the meniscus while clear oil was in the apparatus and the tube sealed with the cork, can be interpreted in no other manner except as evidence that no evaporation took place. None of the previous workers except Kelly have made provisions to prevent evaporations and Kelly's provisions have been found to be inadequate in this work.

Since viscous oil was also used in the side tube as well as the main tube, and the lag was not more than 20 seconds for a movement of 200 divisions of the meniscus, we conclude that lag has been practically eliminated and largely by the reduction of movement of the side tube liquid to a very short distance which amounts to about 4 mm. Another advantage is that only a small volume (about 0.0012 cc.) of clear liquid is transferred to the main tube over a period of several days.

The observation that the error in reading was less than one tenth percent, appears to be well borne out by the curve of Fig. 7, where the data falls on a smooth curve with very satisfactory regularity.

The chief reason for the success of the apparatus is in the ease with which the manipulations can be made and especially the ease with which the run can be started. The fact that the suspension need not be poured in to a definite level, but can be dumped in and the tube shifted to obtain the desired level of the meniscus, is a most important factor in starting runs.

The reason that the water level of the bath must be kept reasonably constant in order to prevent effect on the position of the meniscus is probably that a slight bending of the pipe support occurs and thereby elevates or lowers the tube.

The importance of temperature control in this apparatus indicates the sensitivity of the apparatus. Incidentally, it emphasizes a point not so well recognized, i.e., with sedimentations of this type, constant temperature is more important than in some other types of sedimentation.

Conclusions

1. The formula proposed by Kelly for use with his sedimentation apparatus appears to neglect the important factor of leakage to the larger tube, when the formula is used to determine weight in suspension directly. A formula is proposed which is believed to be more accurate.

2. If percent settled is calculated directly from the readings, the constants appearing in Kelly's equation need not be determined and the experimental work is considerably simplified.

3. The sedimentation tube proposed by Kelly is not satisfactory for the sedimentation of cement when the bulb used to protect against evaporation is blown in the upper end of the manometer side tube, as this makes the tube more difficult to handle and increases the possibility of spoiling experimental runs.

4. Kelly's tube or modified form of this tube do not entirely protect against evaporation and are not satisfactory for sedimentation of cement, for this reason.

5. The protection bulbs proposed by Kelly, although objected to on the grounds that they increase manipulative difficulties do reduce evaporation to a considerable extent, although not completely.

6. Kelly's tube or any modification of it where the tube contains a side tube in an essentially horizontal position, and where readings depend on the travel of a long column of liquid over substantial distances, is not satisfactory for the sedimentation of cement samples which contain a large proportion of coarse particles and thereby produce rapid movement of the meniscus in the early stages of settling, even when viscous liquids are used as the suspension medium, leading to lag in the side tube readings and thus masking the rates of change.

7. The use of a viscous liquid as the suspension medium requires that means be taken to prevent wetting of the main tube wall above the level of the suspension, for example, when adding the suspension, for if the wall is wet, the liquid drains slowly down and causes erroneous results in the first few minutes.

8. Kelly's tube has the disadvantage that the level of the suspension must be perfectly definite and as exactly as possible to a predetermined mark, otherwise the meniscus will not come to equilibrium in a position to permit

utilization of the scale. Attempts to realize this level in the short time permitted when working with cement, result in many failures and much loss of time.

9. The force by which the meniscus is brought to the equilibrium position in Kelly's tube is very slight and the meniscus is very easily stopped or arrested. With further refinement, it should be possible to reduce arresting of the meniscus but it is likely that there will always be a portion of experimental work lost from this cause.

10. The modified Wiegner apparatus developed in this work entirely eliminates evaporation loss and is the only apparatus for sedimentation which does this successfully. Kelly's tube, which is the only other sedimentation apparatus attempting to prevent evaporation loss, is inadequate for this purpose. If evaporation is not prevented, results of any work done with sedimentation tubes of the Wiegner type are of doubtful value.

11. The modified apparatus has almost no lag and permits the use of viscous liquids in the side tube, approximately 200 divisions of change being produced in less than 20 seconds with a viscous liquid.

12. The measuring error of the apparatus is less than one tenth percent of the total range covered.

13. The apparatus developed in this work is easy to operate and is relatively free from manipulative hazards, due to the fact that the level of the suspension need not be adjusted to any definite value, but the tube is either raised or lowered as required. This is of special advantage in carrying out sedimentations of cement, where a substantial amount of relatively coarse particles cause rapid movement of the meniscus during the early stages of settling, since there is little difficulty in obtaining a reading at the end of the first minute.

14. When using oil as the suspension medium, as was done in this work, very careful control of the temperature is required. A variation of not more than 0.01 C may be permitted.

15. Considerable opportunity is afforded with this modified Wiegner apparatus for the investigation of much more dilute suspensions than have been studied. The microscope can be equipped with an objective to give greater magnification and the movement of the meniscus still further reduced.

Chemical Engineering Department,
Ohio State University,
Columbus, Ohio.

COHERENT EXPANDED AEROGELS

BY. S. S. KISTLER

Introduction

There are few topics in colloid chemistry that have experienced such extensive investigation as that of the structure of gels. Numerous hypotheses have been presented and supported by experimental data of one character or another. Certain aspects of gels have seemed to classify them as solid solutions, others as emulsions, while yet others give strong support to a two-phase solid-liquid structure. Although the latter theory in similar form to that postulated by Nägeli in 1858 has been accepted by most of the foremost colloid chemists, the evidence has not been sufficiently unequivocal to convince all.

The evidence presented in the results of diffusion experiments through gels, the fact that the electrical conductivity, refractive index, and vapor pressure before and after setting are identical, at least in certain cases, and the known facts of syneresis would seem to leave little room for doubt of the two phase nature of gels in general. A theory, in order to be perfectly acceptable must, however, enable verifiable predictions to be made from it.

Thomas Graham[1] showed that the water in silica gel could readily be replaced by organic liquids, and Bütschli[2] demonstrated the same fact for gelatin. Every biologist takes advantage of this discovery in making microscopic sections. In that process the water is successively replaced from the gelatinous tissues by alcohol, xyline and paraffin. The final result is a gel in which paraffin is the disperse phase instead of water. In spite of the commonness of this replacement process and the early date of its discovery, very little of a theoretical nature has been made of it. Theories of the origin of swelling in the elastic jellies very commonly ascribe a high place to osmotic forces, but no explanation is offered for the fact that these same gels retain their swelling, and in fact offer great resistance to compression, when the water is replaced by a liquid such as benzene in which osmotic forces must be negligible owing to the insolubility of the material of the jelly.

Gelatinous membranes such as animal membranes, nitro-cellulose, and cellophane[3] have frequently been used as ultrafilters. In many cases there can be no question but that the membrane acts as a sieve. It has been conclusively shown that the water in these membranes can be replaced by other liquids without impairing the sieve action.[3] The membranous filters have demonstrated particularly well the resistance to compression offered by swollen gels, both in water and in other liquids. Unswollen cellophane will not permit any liquids to pass, and even gases at high pressure pass in scarcely

[1] J. Chem. Soc., **17**, 318 (1864).
[2] "Über den Bau quellbarer Körper," Göttingen (1896).
[3] J. W. McBain and S. S. Kistler: J. Gen. Physiol., **12**, 187 (1928).

detectable quantities. When it is swollen by merely wetting in water, however, it passes many liquids with ease. In both aqueous and nonaqueous solutions the author has conducted filtrations at as high as 120 atmospheres pressure with little evidence of compression of the swollen membrane.[4] An interesting fact is that Rodewald[5] found that starch swelled against 2,500 atmospheres pressure.

Whatever may be the explanation of swelling, the evidence is indisputable that when many gels are once swollen they show a resistance to recompression that is independent of the liquid within their meshes. When once transferred from water to a nonswelling liquid they show very obvious indifference to what liquid it may be.

In the face of what has been presented, the emulsion theory is completely untenable except, perhaps, in some very special cases, so that no further thought will be given to it.

In spite of the above facts, it can still be argued that the liquid is of large importance in the constitution of the jelly. Many chemists are of the opinion that in the hydrophyle jellies much of the water is held as shells surrounding the colloid particles. If such were the case, the mobility of the water should be of a different order from that of pure water. That hydration phenomena exist can scarcely be disputed, but the author[6] has definitely demonstrated that the average viscosity of the water within a gelatin jelly and certain of the inorganic jellies is not widely different from that of pure water. The structure of these jellies, when once formed, is very likely only mildly dependent upon solvation.

Such facts as those above, and others, have led me to the conviction that when once formed, a jelly is in general independent of the fluid filling its meshes, and this fluid might just as well be a gas as a liquid. The fact that all coherent jellies are filled with a liquid is accidental and of little significance.

In support of this assumption, one immediately recalls that silica, alumina, and ferric oxide jellies may be dried to a hard glassy mass which is yet porous and undoubtedly retains a vestige of the original structure. Even gelatin jelly that has been transferred to alcohol or benzene shows the same phenomenon.[7] It might be argued that the relationship here is extremely distant. Still a further bit of evidence comes to the support of the assumption. Bechhold[8] and others have been in the habit of measuring the pore diameter of a membrane for ultrafiltration by means of the so-called bubble test. The membrane is supported with water above it and air pressure applied below until bubbles begin to form on the upper side. From the known surface tension of the water and the measured pressure, the diameter of the pore can be calculated. With number 600 cellophane, copious bubbling occurs at pressures below 70 at-

[4] J. W. McBain and S. S. Kistler: Trans. Faraday Soc., **26**, 159 (1929).

[5] Rodewald: Z. physik. Chem., **24**, 193 (1897).

[6] S. S. Kistler: J. Phys. Chem., **35**, 815 (1931).

[7] Bachmann: Z. anorg. Chem., **100**, 1 (1917).

[8] Z. physik. Chem., **60**, 257 (1907). An error in Bechhold's calculations was corrected by S. L. Bigelow and F. E. Bartell: J. Am. Chem. Soc., **31**, 1197 (1909).

mospheres. If the pressure is released, the passages refill with water and it again requires the same pressure to start bubbling. The membrane is found to have suffered no deterioration by the experiment. Now it was shown earlier that a collapsed membrane of cellophane would not permit any gas to pass, so that the only conclusion to be drawn is that the water has been forced out of the meshes of the gel in a small area, and in that region we have a gel with air as the continuous phase.

If one chooses to produce an aerogel by replacing the liquid in a gel with a gas, it is found that as the liquid is evaporated, the gel collapses until it has been reduced to a mass very small compared with the original gel. The very apparent explanation is that as the surface of the liquid tries to recede within the structure of the gel, the capillary effect combined with the high tensile strength of liquid crushes the gel to the point where the structure is strong enough to withstand the force. With unhardened gelatin that point is not reached until practically all of the liquid is gone, while with silica and similar gels complete collapse does not occur and a porous mass remains. Obviously if one wishes to produce an aerogel, he must replace the liquid with air by some means in which the surface of the liquid is never permitted to recede within the gel.

Experimental Procedure

If a liquid is held under a pressure always greater than the vapor pressure, and the temperature is raised, it will be transformed at the critical temperature into a gas without two phases having been present at any time. Actually under these conditions there is no transformation at the critical temperature. The change that does occur is gradual and continuous over the entire range of temperature, and a small increase in temperature from slightly below the critical temperature to slightly above has no more meaning to a gel in the liquid than a similar change in temperature any other place in the temperature range. Accordingly, it becomes possible to take a gel filled with a liquid, transform the liquid gradually into a gas, allow the gas to expand above the critical temperature, and end with the gel filled with gas of low density without at any time having subjected the gel to compressive forces. This, in general, is the procedure that has been followed in the present investigation.

A small autoclave of 75 cc. capacity, capable of withstanding at least 300 atmospheres pressure, was used. It was heated in an electric furnace.

At first the attempt was made to work with the inorganic jellies filled with water. Both the pressures and temperatures are inconveniently high, but a more serious difficulty was encountered. At temperatures approaching the critical, water becomes such a powerful solvent and peptizer that gels such as silica and alumina were completely peptized. At first it was thought that the peptizing action was due to alkali from the glass vessels containing the gels within the autoclave. Careful elimination of this source of alkali did not prevent the peptization, however. For example, a piece of silica gel would go into solution as the temperature rose and later when the density of the solvent became too low would precipitate as a very voluminous powder. The powder

thus formed was undoubtedly crystalline, although no attempt was made to prove it other than to show that adsorption of water vapor in it was negligibly small as compared with adsorption in normal silica gel.

With the inorganic gels it was found satisfactory to replace the water with 95% ethyl alcohol. Occasionally they were transferred from the alcohol to ethyl ether because of the lower critical temperature and of the smaller chemical activity. The organic gels were always transferred from alcohol to ether, thence to petroleum ether and finally to liquid propane, except in the case of nitrocellulose which, on account of its solubility in alcohol and ether, was formed in benzene and transferred directly to the petroleum ether.

The principal precaution to be taken at this stage is always to replace one liquid with another with which it is completely miscible. If the two liquids are not miscible, an interface forms between the liquid in the gel and that outside and can, under circumstances, compress the gel just as a liquid-gas interface does when the gel is dried. Usually it merely serves to prevent exchange of the liquids.

In the present study only firm jellies were investigated since it seemed probable that they would be more independent of the liquid than the gelatinous precipitates. Also the optically clear jellies lend themselves better to observations on internal changes.

Results

Silica. Silica gels were chosen to experiment with first because of the ease of preparation and the mechanical character of the product. The gels were usually prepared by pouring slowly with stirring a solution of "N" brand water glass of specific gravity 1.15 into an equal volume of 6 N hydrochloric acid. The solution was then filtered and set in paraffined crystallizing dishes to harden. After 24 hours sufficient syneresis had set in to loosen the gels from the dishes and enable them to be removed and placed in wash water. Washing was continued until the water showed no chloride ion.

The biologists' experience is that sudden transference of tissues into alcohol produces large shrinkage and distortion. With this in mind, two samples of gel were chosen from the same batch, one was placed immediately in 95% alcohol and the other was transferred by gradual stages extending over several days. The percentage silica in the two resulting alcogels was identical, showing that sudden transfer is quite satisfactory. None of the inorganic jellies used required gradual transference.

The whole cycle of heating to the critical temperature and liberating the gaseous alcohol usually took about an hour and a half. Probably no significance should be attached to the time involved.

The aerogel obtained is transparent and highly opalescent, and occupies nearly the same volume as the aquogel.

The aquogel produced as above contains about 8% silica, so that allowing for about 20% volumetric shrinkage upon removal of the alcohol, and assuming a density of 2 for the silica, the aerogel consisted of 5% SiO_2 by volume, and the remainder air. The structure is so fine, however, that the aerogel is

quite transparent, transmitting light of a slightly orange tint due to the very pronounced scattering that occurs on account of the inhomogeneity of structure. The scattered light is bluish, as would be expected. The aerogel shows considerable resistance to crushing, considering its low percentage of silica, and is quite resilient. When a small piece is dropped, it emits a metallic ring and bounces without fracture.

This material should prove excellent for ultramicroscopic study of gel structure on account of the very large difference in refractive index between phases. An examination of a piece with 1700 diameters magnification and horizontal illumination showed nothing but uniform light due to the Tyndall Effect. Even with thin fragments obtained by fracturing a piece of the silica aerogel the thickness was so large that it was likely that the uniform Tyndall light masked fine structure that might otherwise have been visible. Accordingly, silica gel was cast under a cover glass on a microscope slide and converted into aerogel in the usual manner. Numerous points of light were visible with transverse illumination, but nothing could be seen of what might be called a structure.

Substage transverse illumination proved impractical on account of the small refractive index of the aerogel. The light is completely reflected at the surface of the slide and does not penetrate into the gel. Perhaps some interesting observations could be made with the aid of the new Spierer lens. My cursory microscopic examination proved too meager for any conclusions.

Since silica aerogels are so easy to obtain, a more detailed study was made of them than of any of the other aerogels produced. It was found possible to produce silica aerogels with any percentage silica by volume from 2% up to the dense product of commerce without special precautions, and I feel certain that 2% is not the lowest obtainable concentration. For gels above 5% silica, the usual procedure was to precipitate a gel as described above and then dry it slowly until the desired concentration was reached. Such a dried gel shows very decided evidence of the compression to which it is being subjected. Upon placing it either in water or in alcohol it reswells to a certain extent dependent upon the concentration of the silica, and perhaps upon details of past history. The elasticity of the silica fibrils is very well shown by this effect. The second column of Table 1 shows the increase in volume upon placing pieces of gel in

TABLE I

% SiO_2 by wt.	Percentage change in volume	
	upon placing in alcohol	upon removal of alcohol
8.3	—	−28.1
8.3	+ 2.7	−12.0
9.7	+ 3.7	−22.5
13.6	+ 4.7	− 1.2
17.8	+ 9.6	− 0.7
20.7	+12.2	− 0.9
23.7	+ 9.7	− 1.7

95% alcohol after drying them from an original concentration of 8.3% by weight to the weight percent shown in the first column. Volumetric changes were computed from measurements of linear changes.

Column 3 of the table shows the changes in volume upon conversion into aerogels. In each case the temperature at which the alcohol was released from the autoclave was approximately 20° above the critical temperature.

Initial measurements on the gels were made up to a concentration of 70%, but unfortunately the higher members of the series were accidentally destroyed. It seems reasonable to assume that the increase in volume upon placing in alcohol will decline with the higher percentages of silica.

Unless the autoclave is evacuated after release of the alcohol vapor and while still hot, considerable quantities of alcohol remain within and are adsorbed by the gel upon cooling. It is highly possible that the capillary effect of this alcohol is responsible for part at least of the shrinkage observed. That this alcohol is held as capillarily condensed liquid seems certain from the fact that if the aerogel is heated to 300° or so for a short time in the air it becomes very much more transparent. If the gel is then allowed to stand exposed to the air at room temperature for a few hours, the opacity increases markedly. Transparency is again recovered upon heating. Undoubtedly here and there through the gel small capillaries become partially filled with liquid and offer discontinuities of a larger order, thus increasing very much the scattering of transmitted light. Increase in intensity of the scattered light is very marked when water vapor amounting to only two or three percent of the weight of the silica has been adsorbed.

From 3 to 4 percent of the weight of the aerogel dried at 350° is water that is removed only at a much higher temperature. Probably this water is adsorbed on the surface of the fibrils as a monomolecular layer. However, I have no reason for believing that none of it is held in chemical combination.

The aerogel can be heated to 700° for considerable periods without change in appearance. When the temperature goes to 900°, some internal change takes place that greatly increases the opacity of the product. Although some shrinkage occurs upon such ignition, the aerogel is still of low density and capable of adsorbing much water vapor. Table 2 gives increase in weight with time, of two samples of gel placed in saturated water vapor. Sample 1 was ignited at approximately 800°, while sample 2 was unheated.

TABLE II

Time	Gain in weight	
	Sample 1	Sample 2
3 days	57%	50%
14 days	157	120
23 days	194	140
placed in water	327	166
Total decrease in vol.	67	81

It is very evident that igniting the gel hardened its structure so that it was very much better able to withstand the compressive forces exerted on it as the capillaries filled with water. The final volume of a gram of sample 1 was 73% larger than the volume of an equal weight of sample 2.

Since surface tension is the principal force tending to collapse a gel, the experiment was tried of heating silica gel in the autoclave to a temperature below the critical temperature and releasing the alcohol. The autoclave was heated to 215°, 28° below the critical temperature. Here the surface tension is small but not negligible, being approximately 12% of the tension at 20°. The result was that a good grade of aerogel was obtained, but it suffered a decrease of 52% in volume and was considerably cracked.

Since the structure of the aerogels is submicroscopic, it is to be expected that they can be ground to an exceedingly fine powder. A piece crushed between the fingers has an unctuous feeling like talc or graphite, rather than the gritty feeling that one expects from silica. Ground in a mortar, the powder occupies as large a volume as the original sample, showing that the structure has been very little damaged. Both microscopic examination of the powder and sedimentation measurements indicate many particles of from 1 to 4 microns diameter. Even those of 1 micron diameter must possess a gel structure and be capable of very much finer subdivision.

Alumina. Considerable difficulty was experienced in producing good transparent alumina jellies of sufficient concentration to possess the mechanical strength necessary to assure ease of handling. The method finally adopted was to precipitate the jelly from a colloidal solution of aluminum oxide made by the dialysis of a solution of aluminum acetate (Gann's method). If dialysis was carried far enough, a very small amount of sulfate ion was sufficient to cause a 1% sol to gel. After gelation, the gel was allowed to dry down to the desired concentration. It was found impractical to wash out the small quantity of sulfate on account of the peptizing action of pure water. The attempt was made to wash the gel in dilute alcohol solution in order to prevent peptization. The lump of gel swelled, showing distinct evidence of laminations running parallel to the surface of the test-tube in which it was cast. It then disintegrated into elongated transparent platelets whose lengths were several times their breadths. With a little agitation, the whole mass was completely peptized.

When the desired concentration was reached, the gel was transferred to 95% alcohol and after suitable time had elapsed for the exchange of the water and the alcohol, the alcohol was removed in the autoclave.

The lowest density aerogel so far produced was one of alumina in which the apparent density measured 0.02 grams per cubic centimeter. If one accepts the value for the density of amorphous aluminum oxide as 2.6, that means that in one cubic centimeter of transparent aerogel there was but 0.008 cc. of solid. Needless to say that the gel was exceedingly fragile.

Since with the dilute gels density determinations by means of the displacement of mercury were impractical on account of the danger of crushing the gel, densities were regularly determined by measurement of the displace-

ment of hour-glass sand. The method does not yield highly accurate results, but for rough measurements it is quite practical.

Tungstic Oxide. The attempt was made to produce an aerogel of tungstic oxide. The gel was precipitated from 12% sodium tungstate by means of 6N HNO_3. It was a light yellow opaque gel with very little mechanical strength. It was cast in short sections of wide glass tubing in order to support it during the processes of washing in water, transference to alcohol, and removal of the alcohol in the autoclave. At the critical temperature, alcohol was found to reduce it badly, so that it was found advisable to transfer from the alcohol to ether before placing in the autoclave.

The final product was bluish in color. It occupied the same volume that the aquogel had occupied and seemed to have lost little of what strength it had originally. The forces between the micelles seem particularly weak. It is highly possible that with a study of the conditions of formation, a very much stronger gel could be obtained.

Ferric Oxide. A ferric oxide sol was made by adding ammonium carbonate to ferric chloride, dialyzing for four weeks and then concentrating at a low temperature on the water bath to a syrupy liquid analyzing 8.8% Fe_2O_3. To a part of this sol a dilute solution of potassium sulfate was added a drop at a time with violent shaking between additions until upon standing for half an hour a firm vibrating jelly formed. The remainder of the sol was placed in a test tube and heated in a beaker of boiling water. In the course of half an hour it had set to a firm jelly resembling in every way the one precipitated with sulfate. These jellies were clear and transparent in thin sections. Both were placed immediately in 95% alcohol.

Several attempts to obtain a clear aerogel directly from alcohol met with complete failure. The product each time was a red, opaque, pulverulent mass. Transferring the gel from alcohol to ether and removal of the ether in the autoclave proved equally unsuccessful. Finally by transferring to ether, then to petroleum ether and finally to propane and removing the propane in the autoclave, a good grade of aerogel was obtained. The pieces had small mechanical strength, were very dark red and transparent in thin sections. The density measured 0.2.

At first it was thought that the gel structure must be composed of a hydrate, and the failures in alcohol and ether could be attributed to dehydration at the higher critical temperatures. It was found, however, that the aerogel formed in propane could be heated to 400°-500° without any evident change in structure so that the hydrate hypothesis became untenable. Perhaps the explanation will be found in chemical changes due to the alcohol or water. Even in the ether there were undoubtedly traces of both water and alcohol.

Stannic Oxide. A sol of stannic oxide was made by the hydrolysis of stannic chloride and the peptization of the precipitate with ammonia. Upon slow evaporation, the sol set to a firm jelly. This jelly was allowed to concentrate by evaporation. It was then washed free of most of its water in 95% alcohol, transferred to ether, and the ether removed in the autoclave. The

aerogel formed was slightly tinged with yellow, opalescent and beautifully transparent. Its density was not measured but was estimated to be well below 0.1. Heating to 400° for two hours caused no visible change.

Nickel Tartrate. Nickel tartrate was dissolved in ammonium hydroxide solution and set in an open crystallizing dish to permit the ammonia to evaporate. By slight variations, it was found possible to produce gels that analyzed only 0.14% NiO. The gel from which the aerogel was made analyzed 2.09% NiO. It was demonstrated, however, that the gel substance was actually nickel tartrate so that the gel contained 5.8% solid. It was light green, firm and quite transparent.

Samples were converted into aerogels from both alcohol and ether. That from the latter liquid was the most transparent. The aerogel from both solvents was very fragile. Parts were opaque but many fragments had good transparency, showing that the submicroscopic structure persisted after removal of the liquid.

Cellulose. In spite of the complete success with the inorganic jellies, it remained doubtful if the elastic jellies would yield aerogels. Having studied the properties of cellophane a good deal and having been impressed with the resistance that it offers when swollen to compression either in aqueous or non-aqueous solutions, I felt more sure of success with it than with gelatin. Preliminary experiments trying to obtain swollen cellophane as an aerogel from ether failed. Failure might well have been due to the high critical temperature of ether, 193.8°. Cellulose rapidly undergoes chemical changes at that temperature.

It was thought that perhaps a small amount of residual moisture might have an effect, so some swollen cellophane was extracted with ether in a Soxhlet extractor for several hours, keeping a copious amount of fresh, fused $CaCl_2$ in the distilling flask. The ether was then replaced by propane and the propane removed at 115°. The cellophane was found to have retained its swelling. It appeared white to reflected but translucent to transmitted light. Upon wetting, it became transparent, and during subsequent drying it shrank to its original thickness and had the appearance of ordinary cellophane.

A solution of viscose was made by xanthating cotton. It was filtered and allowed to stand in the laboratory until it gelled (about a week). The jelly was sliced, washed, transferred to propane in the same manner as the cellophane and the propane removed in the autoclave. The product was dense white and was translucent only in thin layers. Its mechanical strength was poor. The probabilities are that if the jelly had been precipitated with electrolyte after the manner of the formation of cellophane or rayon, it would have possessed much more strength as an aerogel. A piece of this cellulose aerogel was set in a watch glass with enough oil to surround it but not to cover it completely. In the course of a short time the oil had displaced the air completely, leaving a transparent jelly of cellulose and oil.

Nitrocellulose. Enough collodion (du Pont's Parlodion) was dissolved in a 50-50 mixture of alcohol and ether to make a very viscous sol. This was poured into a crystallizing dish, a piece of filter paper laid on the surface of the

sol to prevent convection currents, and covered with benzene. In the course of a few days the entire mass of collodion sol had set to a firm jelly. This was sliced, washed in benzene for several days, then in petroleum ether and finally transferred to propane. The propane was changed several times before the jelly and propane were placed in the autoclave.

The aerogel was very light and tough. It had suffered no shrinkage in the autoclave as far as could be told, but was far stronger than the jelly in benzene. It was translucent even in pieces several millimeters thick. It offered large resistance to compression, but when once compressed it did not reswell to its original thickness. This is the strongest and toughest aerogel that has so far been produced.

Gelatin. When it was attempted to transfer a 5% gelatin jelly to alcohol, it was found practically impossible to make the transfer without large shrinkage and the gelatin's turning opaque. By hardening the jelly first with formaldehyde and transferring to alcohol containing formaldehyde by gradual stages, it was possible to replace the water with alcohol without much shrinkage, and the alcogel was semitransparent. It was much easier to obtain a good alcogel starting with 20% gelatin jelly.

Transference was made to propane in the same manner as with cellulose. It was found particularly necessary to reflux in dry ether to remove the small residue of moisture, since otherwise at the temperature reached in the autoclave (105°) the gelatin would become a viscous liquid and when the propane was released it would swell up like a marshmallow.

The aerogel from 20% gelatin showed no signs of having shrunk in the autoclave. It was white, strong, hard and brittle, and was completely opaque except along thin edges. That from the 5% jelly hardened with formaldehyde was dead white and resembled strong pith in its physical characteristics.

Agar. A 4% agar jelly can be transferred immediately to 95% alcohol without evident shrinkage. The jelly in water is translucent, and retains the same appearance in alcohol. The aerogel was very readily obtained after the manner of cellulose and gelatin. It was dead white and had the characteristics of soft pith.

Egg Albumin. An egg was hard boiled and the white converted to an aerogel in the same manner as above. The aerogel was dead white, hard and brittle. It had relatively little strength and could be fairly readily crumbled in the fingers.

Rubber. Swollen rubber is a jelly of a very different nature from those described above. It would be very interesting indeed if it could be shown that rubber could be converted to an aerogel in the same manner as the aquogels. Immediately, difficulties were met that place rubber in a class by itself. The first step necessary in the formation of an aerogel is the replacement of the swelling solvent by an inactive solvent with a sufficiently low critical temperature. It was immediately found, and the experience is not new, that as soon as it is attempted to replace the swelling solvent with a non-swelling liquid, the rubber shrinks down to its original volume.

My observations would favor the theory that rubber is a two-phase system, one phase being a network or sponge of crystalline fibers and the other being a very viscous liquid held within the network. A swelling liquid would then dissolve in the liquid phase and distend the rubber. The attempt to replace the swelling by a non-swelling liquid would result merely in washing the swelling liquid out of the rubber, rubber and the non-swelling liquid being immiscible.

This theory would predict that if one should swell rubber in such a liquid as ether and then cool to a sufficiently low temperature, the liquid phase of the rubber might be precipitated out on the crystalline skeleton and leave an open gel structure similar to that found in the aquogels. It would then be possible to replace the ether with a non-swelling liquid, e. g., alcohol.

This experiment was tried, cooling the ether gel to the temperature of solid carbon dioxide. As was expected, it now became possible to replace the ether with alcohol, and upon warming to room temperature the alcogel of rubber persisted. In the course of a day or two the rubber had driven out the alcohol and consequently had shrunk to something like its original proportions.

Unvulcanized rubber was used in this experiment. The probabilities are that vulcanization would increase the permanence of the alcogel.

An attempt was made to produce an aerogel by swelling rubber, transferring to liquid carbon dioxide and removing the CO_2 above its critical temperature. This undertaking ended in failure, as was expected. The CO_2 dissolves in the rubber, and when the pressure is released instead of diffusing out through the meshes of a gel structure it must diffuse through the viscous liquid phase. The consequence was that many gas bubbles were formed within the rubber, and these decreased in size only slowly.

I am of the opinion that a good rubber aerogel can be made by swelling vulcanized rubber, cooling it to the point where good replacement of the swelling by a non-swelling liquid can be effected, eventually filling the structure with such a substance as liquid nitrogen, that has a critical temperature so low that the rubber is still rigid, and allowing the nitrogen to escape above its critical temperature. The surface tension of nitrogen is so low that the rigid rubber gel might not be much compressed if the nitrogen were merely allowed to boil off.

One possibility remains untried. Rubber gels formed by vulcanizing rubber solution are reported to synerize. If such is the case, it is very likely that the vulcanization has produced the open sponge structure and that with these gels replacement of the solvent can be effected without recourse to low temperatures.

A remark should be made on the effect of rewetting and drying aerogels. In the case of each organic gel, water drew itself through in a few minutes, and the wet gel was then more or less transparent. On drying, the gel shrank to a small horny mass. Directly wetting the inorganic aerogels was usually disastrous, the gel being crushed. On the other hand, if the aerogel was left in saturated vapor until it had had time to partially fill with water, it could then be placed in liquid water with no harm. Subsequent drying caused large

shrinkage, but usually not to the point to which the original aquogel would have shrunk had it been dried. The greater strength of the gel after it has been converted to an aerogel is doubtless due to dehydration of the fibrils.

Discussion and Conclusions

From the number and variety of gels produced, it is evident that the ability to form an aerogel is a general property of gels. It seems that if there are cases in which it proves impossible to convert a normal gel into an aerogel, these cases will be the exceptions.

The formation of aerogels offers a new means of studying the structure of gels. Diffusion experiments can now be performed with gases instead of with liquids, with the attendant great simplification. In the cases such as agar and gelatin in which the aerogel is not transparent, it is evident that the discontinuities are of a size comparable with the wavelength of light, and therefore a microscopic or ultramicroscopic study becomes possible, whereas in the aquogel in which the refractive indices are so similar, structures may be completely invisible. The removal of the solvent now makes it possible to study the gel structures by means of X-rays without the interference of the solvent molecules, which in many cases scatter the radiation as intensely as the substance of the gel.

The nature of the forces between the micelles probably varies from one gel to another, but it does not seem out of place to speculate on the forces in certain cases. Reasoning from the large strength of silica gels and from the small size of the molecule of silicon dioxide, the conclusion seems necessary that the entire structure is knit together by means of primary valency bonds. Secondary bonds would seem entirely too weak to account for the facts. Very likely the forces that hold together the aerogels made by the coagulation of smokes, are secondary. The silica gel and the smoke gel have strengths of vastly different orders of magnitude. The assumption of primary bonds between silica micelles would connote a crystalline structure to the micelles, a conclusion at which Scherrer[9] arrived from X-ray studies.

On the other hand, it seems more difficult to visualize the existence of primary bonds between molecules of cellulose and its derivatives, but here the length of the molecule and corresponding length of the micelle is sufficient to enable the micelles to interlace to a sufficient extent to give the mass large strength in spite of the weak nature of the secondary bonds. There are two difficulties to this explanation, however, that must be met. When such a substance as cellophane is swollen to twice its original volume and converted into an aerogel, the residual forces between the micelles must be very much reduced along a considerable portion of the length of each micelle. They could retain their original value only where the micelles cross or otherwise come into direct contact. It would seem that the tensile strength of such an aerogel would be very much smaller than that of normal cellophane, while qualitative observations place it in the same order of magnitude.

The second objection to the existence of only secondary bonds between the micelles in cellulose and its derivatives is that if residual molecular forces

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[9] Nachr. Ges. Wiss., Göttingen (1918).

between the micelles could account for the large strength, they would be of such magnitude that upon the removal of the swelling liquid the micelles would be so strongly attracted to each other that they would immediately come together, and it would be impossible to obtain a gel of the original volume filled with benzene or other non-polar liquid, let alone a gel filled with air.

It is plausible that there are spots where the micelles are bound very strongly together and that between these spots there are lengths on each micelle only weakly affected by neighboring micelles. Along these lengths, molecules that are strongly adsorbed by the cellulose can crowd in between the micelles forcing them apart, or in other words swelling the cellulose. Even in the swollen cellulose these spots of attachment will remain attached. Friction between the micelles would account for the resistance to collapse offered by the aerogel.

Such arrangement could explain the brittleness of very dry cellulose and the softening effect of anything contained between the micelles. In the manufacture of regenerated cellulose, lubrication between the micelles becomes important.

A type of gel that deserves consideration here is the thixotropic gel, i.e., the gel that is reversible with mechanical agitation. Two of the gels used, the alumina and the ferric oxide gel, were when first formed thixotropic. The subsequent concentration of the alumina gel destroyed its thixotropic nature, but one can assume that the submicrostructure was very little changed by this concentration. That these two gels were converted to aerogels disproves the hypothesis that they owe their existence to the "ionic cloud" surrounding each micelle[10] as also does it disprove the general validity of the observations of Hauser[11] that during gelatin of a thixotropic gel the particles do not actually touch each other. If that really is the case in the bentonite sols studied, it certainly is not so with alumina and ferric oxide.

In conclusion I should like to express my gratitude to Mr. Charles H. Learned for long hours of patient labor in the laboratory, and also to Dr. J. W. McBain for the loan of apparatus and for kindly assistance and advice.

Summary

It was predicted from general considerations and demonstrated experimentally that in general after a gel is formed the liquid phase is accidental and unnecessary.

Aerogels of silica, alumina, tungstic oxide, ferric oxide, stannic oxide, nickel tartrate, cellulose, nitrocellulose, gelatin, agar and egg albumin were made by removal of the water from the normal gels. Rubber offered difficulties not yet surmounted, but the way has been indicated.

The preparation and properties of these aerogels have been briefly described, and some discussion of structure has been included.

College of the Pacific,
Stockton, California,
        and
Stanford University.

[10] F. Haber: J. Franklin Inst., **199**, 437 (1925).
[11] Kolloid-Z., **48**, 57 (1929).

A COMPARISON OF METHODS FOR THE DETERMINATION OF THE AREA OF ADSORBED MOLECULES IN INTERFACIAL FILMS[1]

F. E. BARTELL AND GUILFORD L. MACK[2]

Introduction

The problem of determining the dimensions of an individual molecule is one that has received considerable attention. There are in general two widely different methods available for attacking this problem. One method is that employed for calculating the dimensions of the molecule from the x-ray diffraction pattern of crystals. This has heretofore been limited in application to solids possessing a crystalline structure. Recently, however, Stewart[3] by means of refined methods of measurement, has applied this method to liquids. The other principal method of attack is from the standpoint of surface chemistry. The thickness of films may be determined and calculations may be made from molecular volume data for the area of the molecule.

Surface films are of two types, namely: those formed by insoluble highly adsorbed substances and those formed by soluble and less strongly adsorbed substances. The former may be investigated by measurement of so-called surface pressures and the latter by measurement of surface or interfacial tension. Calculations of molecular area by this latter method have been accomplished (a) by the limiting slope method of Langmuir[4] or by the similar maximum adsorption method as used by Harkins and Wampler[5] and (b) by application of the mixture law method of Mathews and Stamm.[6]

In the present research interfacial tension measurements of water against binary organic liquid systems were made. Calculations of molecular area were carried out by, (a) maximum adsorption method, (b) the mixture law method, and (c) a modified mixture law method.

Methods for Calculation of Molecular Area

The methods above mentioned for the determination of the areas of molecules in soluble films entail the determination of interfacial tension values with which, by means of the Gibbs formulation, $q = - \dfrac{1}{RT} \dfrac{dS_{23}}{d\ln c}$, the areas can be

calculated. In this formulation q represents the mols adsorbed per square cm., and S_{23} the interfacial tension in dynes per cm; the other symbols have their usual significance. Mathews and Stamm have obtained interfacial tension data and have made use of both the limiting slope method and the mixture law method. The agreement of the values thus calculated was only fair.

Maximum Adsorption. The maximum adsorption method is based upon the principle first pointed out by Langmuir, that when the slope of the S_{23}, ln c curve becomes constant, q (the amount of solute adsorbed) is at its maximum value and is independent of concentration. This maximum value of q, which we shall represent as q_L is supposed to represent the number of molecules necessary to form a completely saturated surface layer of adsorbed molecules. Since q_L is expressed in mols/cm², $1/Nq_L$ (N = Avogadro number) gives the number of square cm. per molecule, or the effective area occupied by the individual molecule.

Mixture Law Method. The mixture law as related to surface tension has generally been stated, in effect, as follows: the surface tension of a binary solution is a linear function of the concentration. Mathews and Stamm considered that the law would be equally applicable to the similar interfacial tension relationships and assumed further that the interfacial tension value of a binary solution against water is a linear function of the concentration *in the interfacial layer*.

The mixture law method of Mathews and Stamm involves the use of the interfacial tension-concentration graph and is dependent on the validity of the mixture law. If on this graph a straight line is drawn between the interfacial tension values of the two pure constituents, this line is assumed to represent the concentration of the interfacial film of the mixtures at the corresponding interfacial tension values. The horizontal distance between a point on this line and the corresponding point on the determined interfacial tension-concentration curve is assumed to give a measure of the excess concentration at the interface. This gives, then, the excess surface concentration in mols/cm³. From the Gibbs adsorption equation, the number of mols adsorbed per square centimeter of surface may be calculated. Dividing the latter number by the former gives the thickness of the surface film in centimeters. The dimensions of this equation are:

$$\frac{mols \times cm^{-2}}{mols \times cm^{-3}} = cm.$$

If the film consists of a monomolecular layer of oriented molecules, this gives directly the length of the individual molecule. Its area is calculated by means of the equation $a = M/Ndt$, in which d represents density, and t, the thickness of the film in cm. M and N have the customary significance. In carrying out the calculation it is necessary to make the further assumption that it is justifiable to apply density measurements, which are properly a function of the liquid in bulk, to discrete particles of molecular dimensions.

It should be pointed out that Langmuir had previously employed for the calculation of molecular area a special case of this method which was later

developed more generally by Mathews and Stamm. The equation for calculating the thickness of the surface layer was first given by Langmuir in the form:

$$t = q/(c' - c)$$

In this equation c' represents concentration in moles per liter at the surface, and c the concentration in moles per liter in the bulk of the solution. The surface tension values of water and ethyl alcohol are raised by the addition of soluble salts, hence these solutes must be negatively adsorbed. In other words the solvent is preferentially adsorbed, and hence, it follows that the surface layer consists of molecules of pure solvent, and the concentration of solute in the surface, c', becomes zero. This condition then leads logically to a method for determining the area of the *solvent molecules*. In contrast to this the method applied by Mathews and Stamm gives the area of the *solute molecules*, since in their work the solute is preferentially adsorbed. Their contribution consists in the use of the mixture law to evaluate the factor c' in the above equation.

The values obtained by the so-called mixture law method are obviously dependent upon the validity of this law, while the values obtained by the maximum adsorption method are independent of the mixture law. Attention should be called to the fact that the validity of the mixture law has never been logically established, and further, it is a question whether the fractional constituents of a given mixture shall be expressed as volume fractions, as mol fractions, or as weight fractions. Mathews and Stamm justify their adoption of the mixture law on the ground that the same linear relationship has been reported by Worley[1] to hold for the similar phenomena of surface tension. They state that "for constituents of like polarity against air, which have no orienting effect, the relationship was fairly well followed, as would be expected when there was no concentrating in the interface."

Since Worley reported but one case in which the mixture law appeared to hold, general conclusions based upon his results seem questionable.

The Validity of the Mixture Law. The original formulation of the mixture law was proposed by Rodenbeck.[2] Other investigators have attempted to discover a relationship between surface tension and concentration of mixed liquids and the formulations proposed by them vary from the original only in the units used for expressing the concentration of the constituents. Much confusion appears to have existed on this point. Some authors have used mol fraction, others volume fraction and still others weight fraction. None of these authors has really justified the selection of units used by him. A critical and comprehensive review of the literature is given by Morgan and Griggs.[3] They calculated the effect of employing the different units for a large number of systems, and found that the use of weight fraction units gave least deviation from the linear relationship.

[1] J. Chem. Soc., 105, 267 (1914).
[2] Inaug. Diss., Born (1879).
[3] J. Am. Chem. Soc., 39, 2261 (1917).

They used bulk concentration values in their calculations. Since surface tension is primarily a function of surface concentration the use of bulk concentration values would not be justified in establishing a relationship between concentration and surface tension.

Application of the theoretical considerations of Gibbs[1] would show that bulk concentration and surface concentration must in fact be quite different, so that the mixture law as expressed by Morgan and Griggs would not be expected to hold. In conformity with the second law of thermodynamics it must follow that from a binary liquid system, the constituent of lowest surface tension must concentrate at the interface in order that the free surface energy will be at the lowest level possible. Differences in the dielectric moments of the molecules and differences in the internal pressures of the liquids may cut down the adsorption in certain instances, but in any case the relative molecular concentrations in the interface cannot be the same as the relative concentrations in the bulk of the solution. It is not to be expected, then, that the interfacial tension or surface tension should bear any simple relationship to the concentration in the bulk of the solution. The principal objection to the mixture law formulations, as applied to surface tension, is, therefore, that they express the interfacial tension as a function of the bulk concentration and not as a function of the interfacial concentration.

The surface tension relationships calculated by Morgan and Griggs on the basis of weight fraction were interpreted as indicating a fair agreement with the mixture law. In those cases in which one component of the binary system shows a tendency toward strong preferential adsorption a close agreement would not be expected. Those units which will, when plotted, give a marked sagging of the surface tension-concentration curve are likely more nearly correct than those which show an apparent better agreement.

Methods of Testing the Validity of the Mixture Law. A direct test of the validity of the mixture law as applied to interfacial tension relationships presents a problem of great difficulty since no method is available for the accurate measurement of the interfacial concentration. An approximate method for testing this law might be one based upon the fact that of the two methods available for calculating molecular area, one, the limiting slope method, is independent of the validity of the mixture law, while the other method is directly dependent upon it. The values of the molecular area calculated according to the Langmuir limiting slope method may, by the proper selection of components, be used as a basis for comparison of the values found from the other (thickness of film or mixture law) method. By using the different concentration units for expressing the concentration factor a comparison of the values thus obtained with those obtained by the limiting slope method should serve as a means of testing the validity of the mixture law. This should also provide an experimental basis for choosing the correct concentration units.

As has been mentioned above, if the interfacial tension of a binary mixture of liquids is plotted against the concentration of one constituent in the solution, a curve is obtained which usually sags below the straight line drawn be-

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[1] "Scientific Papers," 1, 219 (1906).

tween the interfacial tension values of the two pure constituents. Only a very few cases have been reported in which the interfacial tensions of the mixtures rose above the straight line, and in each of these cases association, ionization, or other intramolecular changes not characteristic of ideal solutions are known to occur. If, in a nearly ideal solution, the interfacial tension of the mixture is greater than the value calculated from the mixture law, it would seem likely that the wrong concentration units have been used. Now if a system is selected whose constituents have similar polarities and interfacial tensions, the adsorption will be small and only slight deviations below the straight line function will be observed.

If the constituents are chosen so that the density and molecular weight ratios are widely different, use of the correct concentration units should give values conforming to the calculated interfacial tension values. If the wrong concentration units are used interfacial tension values greater than the calculated will be obtained and these units will thus be eliminated from further consideration.

Modified Mixture Law Method. It has been shown that the thickness of the surface film, t, may be determined by dividing the excess surface concentration in mols per cm^2 by the excess surface concentration in mols per cm^3. Similarly if the total surface concentration in mols per cm^2 were divided by the total surface concentration in mols per cm^3, this would give another method for determining the thickness of the surface film. The total interfacial concentration in mols per cm^3 is obtained directly from the mixture law and is represented, in the formulation previously discussed, by the symbol c'. The total interfacial concentration in mols per cm^2 is found from q, the increase in concentration due to adsorption, and from the concentration in the surface before adsorption occurs. This latter factor may be assumed to be equal to the 2/3 power of the concentration in the bulk of the solution. The equation for calculating the thickness of the film may be formulated as follows:

$$t = \frac{q + c^{2/3}/N^{1/3}}{c'}$$

Where c = bulk concentration in mols/cm^3
and c' = interfacial concentration in mols/cm^3.

This method of calculation has been designated as the modified mixture law method. A full explanation of this formulation will be given later.

Method for Measurement of Interfacial Tension. The methods available for the determination of interfacial tension have not been so thoroughly tested with liquid-liquid systems as they have for the corresponding liquid-air systems. The validity of the different equations used has not, in all cases, been firmly established. It is therefore not surprising that much of the interfacial tension data found in the literature is considerably in error. If adsorption at the interface occurs, only static methods are applicable. Of these methods, the sessile drop and ring methods are not sufficiently accurate for exact work. The maximum bubble pressure method has not as yet been extensively applied to interfacial tension measurements. There remain, then,

the methods involving the measurement of the drop volume or the capillary rise. The ease of operation, together with the simple and firmly established formulation for calculating the interfacial tension, led to the adoption of the capillary rise method. It was realized, however, that much more care in cleaning the apparatus and in purifying the liquids was necessary in the capillary method in order to obtain results comparable in accuracy with those obtainable with the drop volume method. On the other hand, the density of the organic liquid used need not be known so accurately as in the drop volume method. This is an important factor to consider in dealing with mixed liquids of widely differing vapor pressures.

The method of Bartell and Miller[1] was selected for use in this investigation.

During the progress of this research, it was necessary to determine the interfacial tension of water against several different liquids which were expensive and which were difficult to obtain in large quantities in the pure state. It became highly desirable to develop a method which would require but a small amount of organic liquid for each measurement.

It was found that by making use of two capillaries of different diameters an apparatus could be constructed which would give very good results and which would require not more than about 2 cc. of organic liquid. A detailed description of this apparatus will be given in another paper.

The thermostat employed was an ordinary rectangular brass box of about 15 liters capacity, fitted with plane glass sides. It was equipped with the usual heating and cooling coils. The mercury regulator held the temperature constant to within ±0.03°C. The stirrer was equipped with a convenient switch so that it could be turned off at the moment of making a reading through the telescope of the cathetometer. The vibration of the stirring apparatus often causes such agitation of the liquid surfaces that the position of the wide meniscus cannot be accurately determined.

A 75-watt lamp mounted behind a ground glass screen was used as the source of illumination. A mirror, 2 x 18 inches, was set at an angle of 45° to a line passing through the center of the telescope. It also made an angle of 45° with the ground glass plate which was parallel to the line of sight through the telescope. This method of illuminating the wide meniscii was compared with the methods used by Richards and Coombs[2] and by Harkins and Humphrey.[3] The results obtained were found to agree closely with those obtained by the other methods.

Purification of Liquids. One of the principal sources of error in the determination of surface tension and of interfacial tension values is the presence of capillary-active impurities in the liquids. Thus, strongly adsorbed substances need be present only in infinitesimal amounts in order to produce a marked change in interfacial tension. The capillary height method of measurement used in this work is particularly susceptible to this effect. This method

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[1] J. Am. Chem. Soc., **50**, 1961 (1928).

[2] J. Am. Chem. Soc., **37**, 1643 (1915).

[3] J. Am. Chem. Soc., **38**, 242 (1916).

is much more static than other methods, such as the drop volume or maximum bubble pressure methods, and impurities have more time to diffuse through the liquid and collect at the interface. For this reason, special care was taken in the purification of all liquids used. With one exception, namely toluene, the standards of purity attained are as high as any previously reported in the literature. The physical constants of all the liquids used had been precisely defined by one or more investigators. The following constants were selected for comparison with the best values in the literature as an indication of the purity of the compound. These values were checked within the limit of the experimental error in every case except the one previously noted.

Density. Specific gravity bottles of 25 and 50 cc. capacity with very finely ground glass joints were used in these determinations. The temperature of the measurement was determined with a thermometer certified by the U. S. Bureau of Standards and the variation was not more than ±.02°C. The volume of the specific gravity bottles at each temperature was determined by finding the weight of water contained and dividing by the known density of pure water at that temperature. This gives the absolute volumes reduced to 3.98°C.

The density was found in general to be the most sensitive criterion of purity. Other properties in special cases are better indicators of the presence of small amounts of impurities, but the density is the best single standard. In this connection it should be emphasized that no single physical property is a reliable measure of the chemical homogeneity of a given liquid. Unless the nature and specific effect of the impurities are known, several different and characteristic properties must be determined.

Boiling Point. The boiling points were determined with precision thermometers having a total range of fifty degrees, graduated in tenths of a degree, and calibrated by the Bureau of Standards except where otherwise noted. Every precaution necessary for obtaining the true ebullition temperature was observed and all corrections applied. All values have been reduced to a barometric pressure of 760 mm. of mercury. Where no values of dp/dt in the neighborhood of the boiling point were available, the integrated form of the Clausius-Clapeyron equation was used for the calculation. It was realized that a correct and constant boiling point is one of the least reliable tests of purity. Therefore, the closely checking results obtained for every liquid investigated were not necessarily considered to be proofs of a high degree of purity.

Freezing Points. Because many of the liquids employed in this research have very low freezing points, it was not practical to make these determinations in all cases. The values recorded agree very closely with the best of those reported by other workers, and this may be taken as a quite reliable indication of the absence of impurities.

The liquids used in addition to water were benzene, toluene, ethylbenzene, n-butylbenzene, nitrobenzene, chlorobenzene and dimethyl aniline.

The methods of purification are indicated in Tables I and II. The boiling points, freezing points and density values are given and are compared with a few of the best values from the literature.

The water used throughout these experiments was of conductivity grade. Care was taken to remove all traces of dissolved air and carbon dioxide in order to avoid any changes in density due to the presence of dissolved gases.

TABLE I

| Substance | Method of Purification | Boiling Points °C | | Authors |
		Found	Other Values	
Benzene	Method of Richards and Shipley[1]	80.20	80.20	Young
		80.21	80.20	T. & M. (1926)
Toluene	Same as above without recrystallization	110.72 ±.01	110.7	Young
			110.6	Perkin
			110.46	R. & S. (1916)
			110.80	T. & M. (1926)
Ethylbenzene	Hg, CaCl$_2$, P$_2$O$_5$ fr. two times	136.11 ±.01	136.18	Young & Fortey
			136.1	Mathews
			135.98	Richards & Barry
			136.15	T. & M. (1926)
Butylbenzene	Same as toluene	183.46 ±.10	183.10	T. & M. (1928)
			180.	Reed & Foster
Nitrobenzene	HCl, K$_2$CO$_3$, steam dist., fr., vac. fr. twice, cryst. twice	210.9 ±.1	210.8	Perkin
			209.2	Friswell
			210.60	Louguinine
Chlorobenzene	NaOH, steam dist. twice, CaCl$_2$, P$_2$O$_5$, fr.	132.01 ±.01	132.00	Young
			131.7	Mathews
			132.00	T. & M. (1926)
Dimethylaniline	Method of Nelson and Wales[2]	194.	193	Perkin
			193.1	Kahlbaum
			192.68	Louguinine

[1] Richards and Shipley: J. Am. Chem. Soc., **38**, 989 (1916).

[2] Nelson and Wales: J. Am. Chem. Soc., **47**, 867 (1925).

TABLE II

Substance	Freezing Points °C		Temp.	Densities (Ref. to 3.98°C)		Author
	Found	Other Values		Found	Other Values	
Benzene	5.49 ± .01	5.58	25.13°	0.8732	0.8736	Young
	5.50 ± .01	5.50			0.87351	T. & M. (1926)
		5.493				R. C. & S.
					0.87344	Patterson
					0.87329	Int. Crit. Tab.
			20.15°	0.8783	0.8788	R. & S. (1924)
					0.8790	R. & S. (1916)
					0.8788	Young
					0.87862	Int. Crit. Tab.
					0.87879	T. & M. (1926)
Toluene			25.13°	0.8610	0.86225	T. & M. (1926)
					0.8624	Perkin
					0.8610	Int. Crit. Tab.
Ethyl-benzene			25.13°	0.8625	0.8624	Int. Crit. Tab.
					0.86239	T. & M. (1926)
Butyl-benzene			25.13°	0.8561	0.8563	T. & M. (1928)
Nitro-benzene	5.60 ± .02	5.67				Tamman
		5.7				Hansen
		5.82				Louguinine
			25.13°	1.1980	1.1972	Walden
					1.1983	Perkin
					1.1981	Int. Crit. Tab.
			15.13°	1.2078	1.2080	Int. Crit. Tab.
Chloro-benzene			25.13°	1.1008	1.1008	T. & M. (1926)
					1.1010	Perkin
Dimethyl-aniline	2.25 ± .02	2.5				Menschutkin
		1.96				Ampoula & Rimatoni
			25.13°	0.9518	0.9518	Int. Crit. Tab.

References to the Literature giving the preceding physical constants are listed below:

Ampoula and Rimatori	Gazz., **27**, 51 (1897).
Bramley	J. Chem. Soc., **109**, 454 (1916).
Friswell	J. Chem. Soc., **71**, 1010 (1897).
Hansen	Z. physik. Chem., **48**, 493 (1904).
Kahlbaum	Z. physik. Chem., **26**, 606 (1898).
Louguinine	Ann. Chim. Phys., (7) **27**, 116 (1902).
Mathews	J. Am. Chem. Soc., **48**, 562 (1926).
Menschutkin	Chem. Centr., **1898** II, 479.
Patterson	J. Chem. Soc., **81**, 1097 (1902).
Perkin (1896)	J. Chem. Soc., **69**, 1191 (1896).
Reed and Foster	J. Am. Chem. Soc., **48**, 1606 (1926).
Richards and Barry	J. Am. Chem. Soc., **37**, 998 (1915).
Richards, Carver and Schrumb	J. Am. Chem. Soc., **41**, 2019 (1919).
Richards and Shipley (1914)	J. Am. Chem. Soc., **36**, 1825 (1914).
Richards and Shipley (1916)	J. Am. Chem. Soc., **38**, 989 (1916).
Tamman	"Krystallisieren und Schmelzen," 227 (1903).
Timmermans and Martin	J. Chim. phys., **23**, 747 (1926).
	J. Chim. phys., **25**, 411 (1928).
Walden	Z. physik. Chem., **65**, 141 (1908).
Young	Sci. Proc. Roy. Dublin Soc., N. S. **12**, 374 (1910).
Young and Fortey	J. Chem. Soc., **83**, 45 (1903).
International Critical Tables, III, p. 27.	

General Procedure

The solutions of the organic liquids were made up in all cases by weight. A few of the more dilute solutions were prepared by the method of successive dilutions, but, in general all the mixtures were made up directly from the pure liquids. They were preserved in Pyrex flasks having tightly-fitting ground glass stoppers. In most cases the interfacial tensions were determined within a few days after the solutions were made up. Errors due to changes in concentration by preferential evaporation of the more volatile constituent of the mixture were thus kept at a minimum.

With the Bartell-Miller method the densities need not be determined with extreme accuracy. A reasonable amount of care is necessary, however, in order to cut down the probable error from this source to a negligible quantity. Accordingly the densities of each pure liquid and every mixture were determined in 25 cc. or 50 cc. specific gravity bottles. It is believed that these determinations are not in error by more than ±0.0002 units.

With the double capillary method used by us the density measurements are of decidedly secondary importance. Accordingly the densities of the mixtures were calculated from the volume percent of each constituent present. The density of a mixture of approximately 50 percent composition was determined. This has been shown to represent the maximum deviation from the calculated density.[1] By interpolation the increase in density on mixing could then be determined for each mixture. These corrections very seldom caused any change in the calculated value of the interfacial tension.

Mixtures of nitrobenzene were made up with each of the four hydrocarbons, benzene, toluene, ethylbenzene and butylbenzene. The interfacial tensions of these solutions against water at 25° C were determined throughout

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[1] Brown: J. Chem. Soc., **39** (1881); Linebarger: Am. Chem. J., **18**, 429 (1896).

the concentration range. The interfacial tension values of the mixtures with benzene were also determined at 15° and 35° C; those with toluene at the additional temperatures of 15°, 30° and 35° C. Mixtures of dimethyl aniline were made up with benzene, and the interfacial tension values throughout the concentration range were determined at 35° C. The values obtained at 25° are given in Tables III and IV. The final results calculated from data obtained at the other temperatures are given in Table IX.

The amount of nitrobenzene adsorbed at the interface has been calculated by means of the modified Gibbs equation, $q = -\dfrac{1}{RT}\dfrac{d\,S_{23}}{d\ln c}$. The adsorption from the different solvents is found to increase in the order benzene < toluene < ethylbenzene < butylbenzene; this would be expected from the relative differences between the interfacial tensions of the pure liquids. Because the solutions are so nearly "ideal" it is felt that the adsorption equation should hold reasonably well up to concentrations of fifty percent, at which concentration the maximum value of q is very nearly reached. At higher concentrations the equation obviously fails to express the true values. This will be discussed more fully in a later section.

<center>TABLE III</center>

<center>Adsorption of Nitrobenzene</center>

<center>From Benzene Solution at 25.13°C</center>

Concentration of Solution mols/cc $\times$ 10^{-3}	Nat. Log. Concentration lnC-10	Interfacial Tension dynes/cm.	Slope $\dfrac{d\,S_{23}}{c\ln c}$	Amt. Adsorbed q mols/cm^2
0.0000	——	34.70	0.000	0.0000
0.3355	2.0001	33.80	0.834	0.3364
1.0020	3.0942	32.60	1.360	0.5484
2.485	4.0025	30.67	2.80	1.129
3.877	4.4473	29.32	3.46	1.395
5.742	4.8400	27.79	4.13	1.666
7.480	5.1044	26.70	4.20	1.694
9.736	5.3680	25.73	4.20	1.694

<center>From Toluene Solution at 25.13° C</center>

Concentration of Solution mols/cc $\times$ 10^{-3}	Nat. Log. Concentration lnC-10	Interfacial Tension dynes/cm.	Slope $\dfrac{d\,S_{23}}{c\ln c}$	Amt. Adsorbed q mols/cm^2
0.0000	——	36.30	0.000	0.0000
0.2899	1.8506	35.50	0.822	0.3315
0.4718	2.3411	35.06	1.170	0.4719
0.5678	2.5263	34.06	1.410	0.5685
1.440	3.4569	33.38	2.133	0.8602
2.440	3.9686	31.86	3.668	1.479
6.120	4.9039	28.00	4.605	1.858
9.736	5.3680	25.73	4.780	1.928

TABLE IV

Adsorption of Nitrobenzene

from an Homologous Series of Hydrocarbons at

25.13° C Ethylbenzene Solution

Concentration of solution mols/cc $\times 10^{-3}$	Nat. Log. Concentration lnC-10	Interfacial Tension dynes/cm.	Slope $\dfrac{d\,S_{23}}{d\ln c}$	Amt. Adsorbed q mols/cm^2
0.0000	———	38.39	0.000	0.0000
0.1974	1.4698	37.77	0.464	0.1871
0.3652	2.0850	37.18	1.440	0.5808
0.7264	2.7726	36.04	1.834	0.7396
1.807	3.6839	33.73	3.446	1.390
3.515	4.3492	31.15	4.214	1.699
5.916	4.8698	28.94	4.570	2.206
9.736	5.3680	25.73	5.918	2.387

Butyl Benzene Solution

Concentration of solution mols/cc $\times 10^{-3}$	Nat. Log. Concentration lnC-10	Interfacial Tension dynes/cm.	Slope $\dfrac{d\,S_{23}}{d\ln c}$	Amt. Adsorbed q mols/cm^2
0.0000	———	41.58	0.000	0.0000
0.1968	1.4464	40.23	0.671	0.2706
0.5252	2.4517	38.51	2.553	1.030
1.604	3.5647	35.00	3.916	1.579
3.107	4.2259	32.03	4.770	1.924
6.246	4.9241	28.48	6.135	2.474
9.736	5.3680	25.73	6.355	2.563

Tests of the Validity of the Mixture Law. For this purpose the chlorobenzene-benzene system was selected. These liquids form practically an "ideal solution"; there is no appreciable volume change or heat effect on mixing. One would expect benzene with its lower interfacial tension to be positively adsorbed. Owing to its non-polar nature, however, its preferential adsorption is small. Unfortunately for our purpose the density and molecular weight ratios are not greatly different, so that the calculated difference between the volume fraction and mol fraction of the mixture is small.

Using the mol fraction units several experimental points on the interfacial tension-concentration curve were found to fall slightly above the straight line curve. The differences are so small, however, that they could be attributed to experimental errors. When weight fraction units are used the resulting interfacial tension-concentration curve falls far below the calculated values. When volume fraction units are used a curve is obtained which is slightly below the straight line curve indicating a slight preferential adsorption of benzene as would be expected. The results of these tests are then most favorable to the use of the volume fraction units; they are not, however, to be regarded as being conclusive. Further confirmation of the correctness of these units was obtained in data presented in Table VI, the significance of which will be discussed later. It is evident, however, that the use of volume fraction units yields results which agree among themselves much better than those obtained by the use of mol fraction units.

TABLE V

Test of Validity of Mixture Law

Method of Maximum Limiting Concentration

Chlorobenzene-Benzene System at 25°C

Interfacial Tension dynes/cm.	Weight Fraction Benzene	Mol Fraction Benzene	Volume Fraction Benzene	Limit Fraction Calc. from mixture law
36.72	0.2628	0.3392	0.3099	0.378
35.98	0.5480	0.6359	0.6045	0.607
35.33	0.7577	0.8183	0.7975	0.810
34.96	0.9016	0.9296	0.9204	0.926
34.74	0.9636	0.9745	0.9709	0.992

Correction for Molecules normally present in the Surface.—Langmuir[1] and others have made calculations of molecular area by employing maximum adsorption values of q (i.e. q_L values) and substituting in the equation $a = 1/Nq_L$. These calculations have been based upon data obtained from comparatively dilute solutions.

It appears that this method should not be extended to the more concentrated solutions without taking into account the molecules of adsorbate normally present in the interface before adsorption occurs. The number of molecules thus present in one square centimeter of surface has been assumed to be equal to the two-thirds power of the number of molecules contained in one cubic centimeter of the solution. If c is expressed in mols per cm^3 then $(c N)^{2/3}$ gives the number of molecules lying in a plane of 1 cm^2 area within the solution. This term divided by N(or $c^{2/3}/N^{1/3}$) will give the number of moles per cm^2 initially present in the surface layer.

The total concentration of the interfacial layer should thus be equal to the sum $(q + c^{2/3}/N^{1/3})$.

In the dilute concentration range considered by Langmuir the factor $c^{2/3}/N^{1/3}$ is very small in comparison with q, and lies within limits of the experimental error in determining the latter value. Consequently, it need not be considered in these cases. Harkins and Wampler[2] have recently shown that in several cases the correction becomes appreciable at concentrations of approximately 1 mol per liter. In our work the value of $c^{2/3}/N^{1/3}$ was usually found to be one to two times greater than that of q. Mathews and Stamm made use of the limiting slope method for calculating the area of molecules adsorbed from concentrated solutions but they did not take into account the molecules initally present in the interface. It would seem that this method of calculation should give results several times too large.

An attempt was made in our work to obtain evidence bearing upon this point.

[1] J. Am. Chem. Soc., **39**, 1848 (1917).

[2] J. Am. Chem. Soc., **53**, 850 (1931).

TABLE VI

Molecular Area of Nitrobenzene
Adsorption from Butylbenzene Solution at 25° C.

Mol Fraction Concentration Units

Fraction Nitro-benzene	Slope $\dfrac{d\,S_{23}}{d\ln c}$	Interface Concentration				Thickness of Film cm. $\times 10^{-7}$		Molecular Area cm² $\times 10^{-16}$		
		Total mols/cm³ $\times 10^{-3}$	Excess mols/cm³ $\times 10^{-3}$	Adsorbed mols/cm² $\times 10^{-10}$ (a)	Total mols/cm² $\times 10^{-10}$	(a)	(b)	from Thickness (a)	(b)	Max. Ads. (c)
0.0305	0.671	0.503	0.306	0.2706	0.6704	0.885	1.331	19.2	(12.7)	246.
0.0800	2.553	1.412	0.887	1.030	1.799	1.161	1.273	14.6	(13.3)	91.6
0.2313	3.916	2.878	1.274	1.579	3.198	1.339	1.111	13.7	15.3	51.6
0.4167	4.770	4.485	1.378	1.924	4.439	1.393	0.990	12.1	17.1	37.2
0.7318	6.135	7.04	0.79	2.474	6.481	3.14	0.992		18.4	30.6
1.000	6.355	9.736	—	2.563	7.949		0.817		20.8	30.6

Average 14.9   18.4   Limit 30.6

Volume Fraction Concentration Units

0.0202	0.671	0.808	0.611	0.2706	0.6704	0.443	0.830	26.2	(20.4)	246.
0.0540	2.553	1.889	1.364	1.030	1.799	0.755	0.952	22.4	(17.8)	91.6
0.0647	3.916	4.055	2.451	1.579	3.198	0.645	0.710	26.3	23.8	51.6
0.3190	4.770	5.865	2.758	1.924	4.439	0.698	0.758	24.3	22.4	37.2
0.6415	6.135	8.04	1.79	2.474	6.481	1.382	0.807		21.0	30.6
1.00	6.355	9.736	0.00	2.563	7.949		0.817		20.8	30.6

Average 24.8   22.0   Limit 30.6

The amount of adsorption at the interface was determined by measurement of interfacial tension and application of the Gibbs formulation. The amount of solute present at the interface at each concentration investigated was also calculated. The sum of these theoretically give the total amount of solute at the interface.

Data obtained for a given system are given in the form of a graph in Fig. 1. While the curves shown on this graph have been plotted from actual data, no units have been given in order that the figure may be considered as being applicable to a perfectly general case.
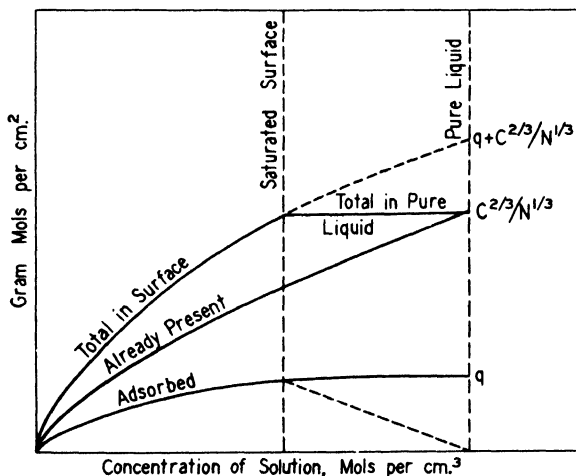
FIG. 1
Molecules of Adsorbate present at an Interface

The lower curve of Fig. 1 represents the number of mols adsorbed at the liquid-liquid interface, as calculated by means of the Gibbs equation. This equation is derived upon the necessary condition that the osmotic pressure within the solution be proportional to the mol fraction of the constituents present[1]. For the nearly ideal solutions used in this work it has been assumed that this condition does hold up to a concentration of one mol per liter, and a close approximation of it may be expected to hold up to four or five times this concentration. This is about the concentration necessary for the production of a saturated surface layer of the solute molecules. In substantiation of the statement that the calculated values of q are approximately correct, it may be pointed out that q has very nearly attained its maximum value at that concentration which is in equilibrium with a saturated interface. Above this concentration the equation fails to express the true values of the adsorption. These deviations will be discussed later.

The middle curve of Fig. 1 represents the number of the solute molecules present in an unit surface assuming they are here randomly distributed as they are throughout an unit volume.

[1] Milner: Phil. Mag., (6) 13, 96 (1907).

Considering a plane in the interior of the solution it seems reasonable to expect that the number of molecules per square centimeter should be equal to the two thirds power of the molecules per cubic centimeter. If this plane be moved into the interface, the perfectly random distribution normally occurring in the bulk of the solution may be affected by the unbalanced surface forces. The solute molecules being, in general, quite polar in nature will be oriented in the interface even when no adsorption occurs. Then, unless the molecules are symmetrical in shape and uniform in all dimensions, the curve will not represent the true number of mols present in the interface.

The upper curve is given by the sum of the values of the two lower curves and represents the total number of molecules at the interface. The upper dotted portion of this curve represents imaginary values, since the surface concentration cannot exceed that found for the pure solute liquid. The calculated total number of mols in the surface is thus in error by at least the amount which is represented by the vertical distance between the dotted line and solid horizontal line representing the number of mols in a saturated surface. This error may be due to errors introduced in either or both of the component parts of the sum. By assuming the $c^{2/3}/N^{1/3}$ factor to be correct, a more probable value of q is obtained which is represented by the lower dotted line shown in the figure. This dotted line together with the first portion of the solid adsorption curve represent the maximum values of q. Ostwald and Izzaguirre[1] as well as several workers in this laboratory[2] have obtained results which indicate that the actual relative adsorption is practically always less than the theoretical maximum values except in the dilute solutions. They obtained an equation which appears to give the correct relative values throughout the concentration range. These corrections could not be attempted in this paper, since no method is available for the conversion of relative adsorption values to absolute values.

Summarization of Methods

In recapitulation the methods available for the determination of area of adsorbed molecules in interfacial films are as follows:

(1) Maximum adsorption method.

The maximum adsorption method as referred to in this paper is based upon the limiting slope method used by Langmuir. In case c (the concentration of solute in bulk) is not negligible in comparision to c' (the concentration of solute in the interface) the number of molecules of solute normally present in the interface before adsorption must be taken into account, the total number of molecules at the interface being represented by the formulation $q_L + c^{2/3}/N^{1/3}$. In the maximum adsorption method the total number of molecules were considered. It follows then that the limiting slope method used by Langmuir and the "maximum adsorption" method used by us differ only by the factor $c^{2/3}/N^{1/3}$ which was used in the latter method.

[1] Kolloid-Z., **30**, 279 (1922); **32**, 57 (1923).

[2] Bartell and Sloan: J. Am. Chem. Soc., **51**, 1643 (1929); Bartell and Miller: Thesis (unpublished), University of Michigan (1929); Bartell and Scheffler: J. Am. Chem. Soc., **53**, 2507 (1931); Bartell, Scheffler and Sloan: **53**, 2501 (1931).

TABLE VII

Molecular Area of Nitrobenzene

Adsorption from Benzene Solution at $25°$ C

Vol. Fraction Nitrobenzene	Slope $\dfrac{d\,S_{23}}{d\ln c}$	Interface Concentration				Thickness of Film cm. $\times 10^{-7}$		Molecular Area		
		Total mols/cm³ $\times 10^{-3}$	Excess mols/cm³ $\times 10^{-3}$	Adsorbed mols/cm² $\times 10^{-10}$ (a)	Total mols/cm² $\times 10^{-10}$ (b)	(a)	(b)	From Film Thickness cm² $\times 10^{-16}$ (a)	(b)	Max. Ads. (c)
0.0345	0.834	0.9975	0.6620	0.3364	0.9068	.508	.909	33.3	(18.6)	181.9
0.1029	1.360	2.335	1.333	0.5484	1.7314	.411	.743	41.2	22.8	95.3
0.2552	2.80	4.450	1.965	1.129	3.296	.575	.742	29.4	22.8	50.0
0.3982	3.46	5.90	2.02	1.395	4.311	.691	.731	(24.5)	23.2	38.2
0.5895	4.13	7.49	1.75	1.666	5.455	.952	.728		23.3	30.6
0.7683	4.20	8.68	1.20	1.694	6.213	1.412	.716		23.6	30.6
1.0000	4.20	9.736	0.00	1.694	7.080		.728		23.5	30.6

Average 34.6 23.2 Limit 30.6

Adsorption from Toluene Solution at $25°$ C

.0297	0.822	0.866	0.597	0.3315	0.8478	.556	.958	30.5	(17.4)	195.
.0485	1.170	1.315	0.843	0.4719	1.188	.560	.904	30.3	18.8	139.
.0583	1.410	1.529	0.961	0.5685	1.379	.591	.902	28.7	18.8	120.
.1478	2.133	2.931	1.491	0.8602	2.367	.577	.809	29.4	21.0	70.
.2468	3.668	4.187	1.785	1.479	3.598		.860		19.7	45.8
.6286	4.605	7.741	1.621	1.858	5.811		.751		22.6	30.6
1.0000	4.780	9.736	0.00	1.928	7.314		.751		22.6	30.6

Average 29.7 20.6 Limit 30.6

TABLE VIII

Molecular Area of Nitrobenzene

Adsorption from Ethylbenzene Solution at 25° C

Vol. Fraction Nitro-benzene	Slope $\dfrac{d\,S_{23}}{d\ln c}$	Interfacial Contentration				Thickness of Film cm. $\times 10^{-7}$		Molecular Area		
		Total mols/cm³ $\times 10^{-3}$	Excess mols/cm³ $\times 10^{-3}$	Adsorbed mols/cm² $\times 10^{-10}$ (a)	Total mols/cm² $\times 19^{-10}$ (b)	(a)	(b)	From Film Thickness cm² $\times 10^{-16}$ (a)	(b)	Max. Ads. (c)
.02028	0.464	0.6281	0.4307	0.1871	0.5877	.435	0.936	38.9	18.1	281.
.03751	1.440	1.042	0.677	0.5808	1.184	.858	1.136	19.8	16.4	139.
.07461	1.834	1.826	1.100	0.7396	1.695	.672	0.928	25.2	18.3	97.
.1855	3.446	3.592	1.785	1.390	3.143	.779	0.875		19.4	52.5
.3609	4.214	5.569	2.054	1.699	4.430	.828	0.796		21.3	37.2
.6097	5.470	7.272	1.356	2.206	6.057	1.627	0.834		20.3	30.6
1.0000	5.918	9.736	0.00	2.387	7.773	.00	0.798		21.2	30.6

Average 27.2   20.1 Limit 30.6

The values of the molecular areas as calculated by this method are given by the reciprocal of the corrected total number of molecules per cm^2 in the interface. This treatment has been previously discussed in connection with Fig. 1.

(2) The mixture law method as used by Mathews and Stamm has been fully discussed and needs no further amplification at this point.

(3) The modified mixture law method has also been discussed. The difference between this method and the mixture law method is brought out by the emphasis given below.

Mixture Law Method   Modified Mixture Law Method
(a)   (b)

$$t = \frac{\text{mols adsorbed}/cm^2}{\text{mols adsorbed}/cm^3} = \frac{\text{total mols in surface}/cm^2}{\text{total mols in surface}/cm^3}$$

$$= \frac{q}{c'-c} \qquad = \frac{q+c^{2/3}/N^{1/3}}{c'}$$

In Tables VII and VIII both of these methods have been used in calculating the molecular area of nitrobenzene, the different columns being labeled as above, (a) and (b) respectively. The third column (c) contains data obtained by the maximum adsorption method. In the same way, a number of other values of the molecular area of nitrobenzene and dimethyl aniline have been calculated. These results are summarized in Table IX.

For the purpose of comparison with the data of Mathews and Stamm a fourth column (d) is included in the table, the values of which have been calculated according to the original limiting slope method when applied to concentrated solutions. It is seen that these values are much too high.

TABLE IX

Molecular Area of Nitrobenzene and of Dimethyl Aniline
A Summary of Values

Nitrobenzene

Solvent	Temperature	Area per Molecule $cm^2 \times 10^{-16}$			
		(a)	(b)	(c)	(d)
Benzene	15°	39.2	23.0	30.4	94.8
”	25°	34.6	23.2	30.6	97.4
”	35°	33.3	22.5	30.8	100.5
Toluene	15°	34.5	21.7	30.4	88.5
”	25°	29.7	21.5	30.6	85.7
”	30°	32.4	21.5	30.7	87.1
”	35°	33.4	20.9	30.8	87.8
Ethylbenzene	25°	27.2	20.6	30.6	69.1
Butylbenzene	25°	24.8	21.0	30.6	64.5
	Average	32.1	21.8	30 6	86.2
Dimethyl Aniline					
Benzene	35°	41.5	26.6	35.5	111.3
Benzene (Mathews & Stamm)	25°	38.4	——	——	75.8
Heptane (” ” ”)	25°	34.8	——	——	57.2

a = area calculated from mixture law method.
b = ”   ”   ”   modified mixture law method.
c = ”   ”   ”   maximum adsorption method.
d = ”   ”   ”   limiting slope method.

Discussion of Results

The results presented in column (a) calculated by the mixture law method are subject to the errors inherent in the modified Gibbs adsorption equation and to the errors inherent in the mixture law method as used.

The results presented in column (b) calculated by the modified mixture law method are subject to all the errors of the previous method and in addition to the error involved in the assumption that the number of molecules originally present in unit area within the bulk of the solution is the same as the number present in unit area of surface.

This method has the advantage over the original mixture law method in that the data obtained throughout the entire concentration range may be used, while the original mixture law method is limited in application to points on the first portion of the interfacial tension-concentration curve in which the maximum adsorption values have not been reached. It is in this range that the absolute values of the quantities from which the molecular areas are calculated are relatively small. Hence, the same experimental error produces a much larger relative error in the calculated value of area than would be obtained by use of the other method. At very low concentrations, low values are obtained by the second method. This may be the result of the relatively stronger tendency for the molecules near the surface to become oriented. The spatial distribution of the molecules will then be furthest from a random arrangement and the calculated value of the factor $c^{2/3}/N^{1/3}$ will be in error by a greater amount with these dilute solutions.

The results obtained in column (c) calculated by the maximum adsorption method show good agreement with the values in column (a). The reliability of the results calculated by the maximum adsorption method is subject to question. This method cannot be considered to compare in accuracy with the similar limiting slope method when this latter method is applied to dilute solutions of highly adsorbable substances. It is evident that the *final* limit value obtained by the maximum adsorption method is independent of the amount of adsorption, and depends only upon the molecular volume of the adsorbed molecules. The arbitrary manner of this calculation throws considerable doubt upon the validity of the results.

None of the methods above described for determining the area of adsorbed molecules are entirely free from theoretical objections. The values obtained and presented in this paper agree among themselves more closely than have values previously obtained by similar methods.

The methods which have so far been used in this paper for the calculation of molecular area, while widely different in many respects, are alike in that they all depend upon surface film measurements. Comparison with the values obtained by Stewart from the totally different method based upon the measurement of the diffraction of x-rays by liquids should provide a good test of the absolute accuracy of the surface film methods. At the same time it furnishes an independent check of the theory of cybotaxis upon which Stewart's calculations of molecular diameter are based. Investigations by the

x-ray diffraction method upon the particular liquids used by us are not available, but values for a sufficient number of substitution products of benzene have been worked out by Stewart to enable one to draw quite definite conclusions as to the most probable dimensions of nitrobenzene and dimethyl aniline. The values given in Table X are compatible in every case with the results presented in this paper.

TABLE X

The Area of Molecules calculated from Stewart's Values
for the Molecular Diameters

Substance	Molecular Diameter cm. $\times$ 10^{-8}	Molecular Area sq. cm. $\times$ 10^{-16}
Benzene	4.70	31.4
Toluene	5.06	34.8
Ethylbenzene	4.99	40.6
Isopropylbenzene	5.36	43.0
Phenol	4.77	30.8
Aniline	4.75	31.8

University of Michigan,
Ann Arbor, Michigan.

MONOMOLECULAR FILMS.* THE SOLID-LIQUID INTERFACE AND THE SEDIMENTATION AND FLOCCULATION OF POWDERS IN LIQUIDS[1]

BY WILLIAM D. HARKINS AND DAVID M. GANS

1. Introduction

While it is known that the volume occupied by a powder after long settling in a liquid is dependent upon the composition of the liquid, the fact that monomolecular films at the solid-liquid interface have an extremely great effect upon the settling, has been unknown. The phenomena of settling in both aqueous and organic liquids present many remarkable characteristics. While experiments in both classes of liquids have been carried out, the present paper will be restricted almost entirely to those of the organic type, since they have revealed more new unknown and striking relations.

The energy of immersion of a solid oxide in the form of a powder, is very low in a non-polar liquid such as hexane, benzene, or carbon tetrachloride. However, if a small amount of an organic acid, alcohol, amine, or any other similar liquid is added to the non-polar liquid, the heat of immersion is greatly increased. Molecules of this type may be designated as hetero-homopolar, and are commonly represented by the symbol, in which the circle represents a polar group.

The data[2] on the heat of immersion indicate that the polar groups in such molecules are oriented toward the oxide at the solid-liquid interface. Obviously the orientation of the molecules in this interface is the same with a pure liquid if its molecules are of the hetero-homopolar type.

The purpose of the work reported in this paper was to determine the effect of such an oriented interfacial film upon the final sedimentation, and upon the rate of sedimentation of a powder in the liquid, since these indicate the extent of the flocculation of the powder.

The presence of a monomolecular oriented film of molecules of the hetero-homopolar type is found to prevent flocculation. If, however, molecules of water are also present, the mixed film does not prevent flocculation to the same extent, and if a considerable amount of water is present in the mixed film, the flocculation may be as great as in a pure non-polar liquid.

2. Experimental Procedure

In a part of the experiments on settling, about 48 cu. cm. of the liquid was drawn by a syphon into a graduated glass-stoppered cylinder and the stopper immediately inserted. The powder, dried at a high temperature in a high vacuum (8.0 grams), was then weighed quickly and poured into the cylinder, exposing the powder to the atmosphere as little as possible. The tightly stoppered cylinders were then vigorously shaken and allowed to stand, and the volume of the suspension read off at intervals. Other more carefully conducted experiments were carried out in sealed pyrex tubes, with special care to exclude moisture, and were used to check the values obtained in the stoppered cylinders.

3. Preparation of Liquids and Drying of Powder

The titanic oxide (TiO_2) used in this work was dried in a high vacuum at 450° to 550°C. for 24 hours.

Thiophene-free benzene was dried over oil-free sodium wire for several weeks. Fresh sodium wire was added several times during this period. The benzene was then distilled, and the distillate stored with a large quantity of sodium wire distributed through its volume.

The oleic acid was purified by the method used by Harkins and Beeman, who applied the well known procedure in which the lead and barium salts are used.

4. An Adsorption Method for the Determination of the Area of the Surface of a Powder

In problems which concern settling or those which involve surface energy it is of fundamental importance to have a method for the accurate determination of the area of the surface of a powder. The method described below is believed to be the most accurate of all known methods.

The powder, titanic oxide or silicon dioxide for example, is dried in a high vacuum at as high a temperature as can be used without affecting the area of the crystals. The cool, dry powder is immersed in a solution of oleic acid, butyric acid, or some other suitable acid, in *very dry* benzene, and the suspension is shaken until equilibrium is attained. After the powder has settled, a sample of the supernatant liquid is drawn off. The benzene of this sample and of a sample of the initial solution is evaporated off, if oleic acid is the solute chosen, and the oleic acid left from each solution is dissolved in 95% ethyl alcohol. The alcohol solutions are then titrated with carbonate free sodium hydroxide dissolved in water. The difference in concentration is considered to give the amount of acid adsorbed by the surface of the powder. Only air that is thoroughly dried by phosphorus pentoxide is allowed to enter the vessel in which the solution is prepared and the flasks in which the adsorption experiments are carried out.

Fig. 1 shows how the amount of oleic acid adsorbed by the surface of one gram of powder varies with the concentration of the final or equilibrium solution of oleic acid in benzene. At concentrations above 0.01 to 0.02 moles per

kilogram of benzene the adsorption becomes practically constant, and the oleic acid on the surface of the grains of powder may be said to form a condensed film. There is some evidence which seems to indicate that this film is monomolecular.

It may be assumed that the area occupied per molecule of oleic acid at the interface is 20.0 sq. Å., which is about the mean value for condensed films of the acid on water at a zero film pressure. On this basis, the area for TiO_2-I was calculated as 22.9 sq. m. per cu. cm. of titanic oxide (3.89 grams), and for TiO_2-II as 14.4 sq. m. per cu. cm. The ratio of these values is 1.59, while
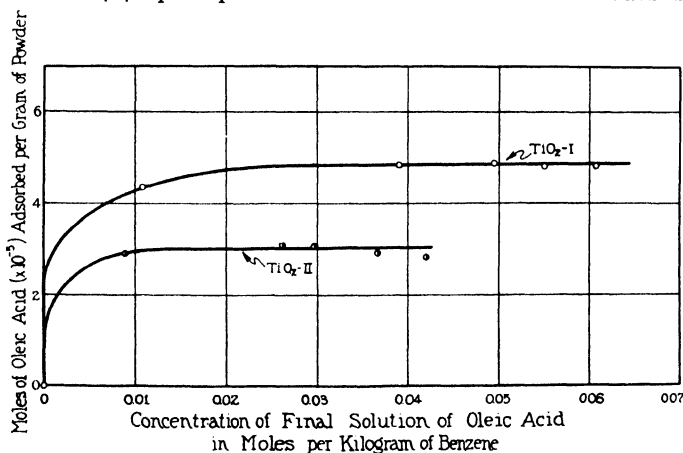
FIG. 1
Adsorption Curves for Dried Titanic Oxides

the ratio for the energy of immersion[1] in ethyl acetate for the same two powders is 1.53, and the ratio of the weights of propyl alcohol adsorbed[2] from the vapor per unit weight of these powders at a constant vapor pressure equal to one-half the saturation pressure at room temperature is 1.53.

The area of the powder TiO_2-II as determined for us by a microscopic method,[3] applicable to crystalline powders, is 13.8 sq. m. per cu. cm. of powder, on the assumption of a spherical shape for each particle. This is in good agreement with the value 14.4 obtained by the adsorption method. However, the closeness of the agreement is to some extent accidental, since the adsorption method includes the area of the colloidal part of the powder, which is not included by the microscopic method. However the agreement between the two methods indicates that the film is monomolecular and not polymolecular.

5. Effect of a Monomolecular Film of Oleic Acid on the Settling of Powders

The experiments described below show that if a powdered crystalline oxide is allowed to settle in benzene the most complete settling is obtained when the grains of powder are coated with a film of oleic acid one molecule thick.

[1] Harkins and Dahlstrom: to be published.
[2] Gans and Brooks: to be published.
[3] Dunn: Ind. Eng. Chem., Anal. Ed., 2, 59 (1930).

A fine powder consisting of titanic oxide was dried in a high vacuum at 400° C. for 24 hours. It was then suspended in extremely dry benzene in tubes about 2 cm. in diameter. After several weeks the top of the powder attained a constant level. The density of the titanic oxide used is 3.89, and so 3.89 g. of the material may be considered to occupy 1 cu. cm. This amount of material was found to settle to a final volume of 20 cu. cm., that is, until 19 of the 20 cu. cm. was occupied by the benzene between the grains of powder.

It was found that if oleic acid was added to the benzene any *initial* concentration up to 0.005 moles per kg. of benzene produced no great effect
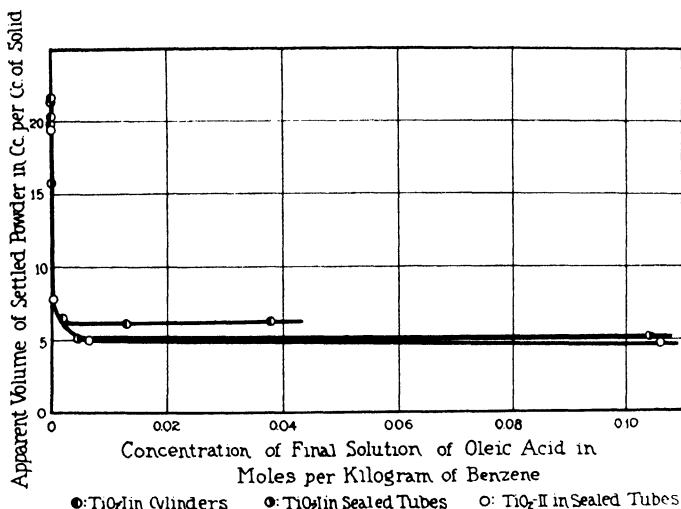
FIG. 2
Variation of Extent of Settling with Amount of Oleic Acid present

(Table I) but a concentration of 0.008 moles of oleic acid gave complete final settling to a volume of 6.5 cu. cm. per cu. cm. of oxide, while if the suspension were kept very dry in sealed tubes as little as 0.0016 moles per kg. of benzene produced settling to 16 cu. cm. per cu. cm. of material with sample I and to 8 cu. cm. with sample II.

It has been shown in Section 5 that oleic acid is highly adsorbed from its solutions in dry benzene by titanic oxide. Harkins and Dahlstrom[1] have shown that this is an effect which is obtained whenever an active or polar group is present in the organic compound used.

The values for the heat of immersion show that the active group is oriented toward the oxide and the non-polar group toward the benzene (Fig. 6). They show that powders which consist of the oxides of silicon, tin, zinc, or of barium sulfate, also exhibit a similar great adsorptive effect.

The effect of the adsorbed film of oleic acid in producing settling is shown by Fig. 2.

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[1] Harkins and Dahlstrom: Ind. Eng. Chem., **22**, 897 (1930).

Thus the presence of 0.005 moles of oleic acid per kg. of benzene in the *final* equilibrium solution is sufficient to cause complete settling, in which the initial volume of 21.5 cu. cm. per cu. cm. of solid in dry benzene alone is reduced by four times to 5 cu. cm.   The addition of larger amounts of oleic acid is seen to produce no further effect.

TABLE I

Apparent Volume of Powder after Settling in Benzene
in Cc. per Cc. of Solid
C = Initial Concentration of Oleic Acid
Moles per Kg. Benzene

A.   TiO$_2$-I in Cylinders

% Water in the Powder	C = 0.0000	0.00145	0.00498	0.00827	0.0208	0.0490
0.00	20.3	21.5	19.8	6.5	6.1	6.3
0.05	20.6	21.9	21.1	20.8	20.1	20.0
0.25	20.7	22.0	22.1	21.6	21.7	21.5
0.95	22.2	22.1	22.1	21.6	21.8	22.0

B.   TiO$_2$-I in Sealed Tubes

% Water in the Powder	C = 0.0000	0.0016	0.0111	0.0354	0.1111
0.00	21.4	15.8	5.1	—	5.2
0.05	—	—	—	—	14.4
0.33	—	—	—	18.9	—

C.   TiO$_2$-II in Sealed Tubes

% Water in the Powder	C = 0.0000	0.0016	0.0111	0.0354	0.1111
0.00	19.4	7.9	5.0	—	4.7
0.05	—	—	—	—	9.4
0.33	—	—	—	14.1	—

The curves of Section 4 indicate that at 0.005 moles per kg. of benzene the adsorbed film of oleic acid is monomolecular, but is not quite tightly packed.

It may be noted that the above refers to titanic oxide I or II when extreme precautions were taken to keep both the benzene and the titanic oxide very dry, and when the suspension was kept in sealed pyrex tubes. When the suspension was kept in glass stoppered cylinders an even smaller final concentration of oleic acid (about 0.003 moles per kg. of benzene) gave complete settling, but to only 6 instead of 5 cu. cm.   That is, the minute amount of water which evidently was able to get into the film, decreased the amount of oleic acid necessary in the film and decreased the settling only slightly.   It will be shown in Section 7 that slightly larger amounts of water in the oleic acid film decrease the extent of settling much more.

6. Effect of Vibration on Settling

The minimum volume for one cu. cm. of the solid after settling is found to be about 5 cu. cm. The density of titanic oxide is 3.89 so that the mass of one cu. cm. of the solid oxide is 3.89 grams. The volume of this amount of powder in the absence of the dispersing liquid was found to be 5.5 cu. cm. for TiO_2-I, and 3.5 cu. cm. for TiO_2-II, as obtained by a gentle pressure which was used to remove air pockets. The former of these values is approximately that obtained for the final volume of the suspension, while the latter value is considerably less.

In order to determine the effects of a gentle mechanical agitation upon the suspensions, the sealed tubes were put vertically in a large test tube rack which was caused to vibrate horizontally 400 times per minute with an amplitude of 1 cm. In order to increase the effect the tubes were left loose in the racks. After 30 hours of vibration almost no further settling occurred, but the vibration was continued until the total period was 64 hours.

TABLE II

Effect of Tapping on Apparent Volume of Powder
after Settling in Benzene
C = Initial Concentration of Oleic Acid
Moles per Kg. Benzene

A. Apparent Volume in Cc. per Cc. of Solid

% Water in the Powder	C = 0.0000	0.0016	0.0111	0.0354	0.1111
		1. TiO_2-I in Sealed Tubes			
0.00	8.9	6.5	3.9	—	3.8
0.05	—	—	—	—	5.4
0.33	—	—	—	6.5	—
		2. TiO_2-II in Sealed Tubes			
0.00	8.0	3.5	3.1	—	2.8
0.05	—	—	—	—	3.1
0.33	—	—	—	5.1	—

B. Ratio of Apparent Volume with Tapping to Apparent Volume without Tapping

		1. TiO_2-I in Sealed Tubes			
0.00	0.42	0.41	0.76	—	0.73
0.05	—	—	—	—	0.38
0.33	—	—	—	0.27	—
		2. TiO_2-II in Sealed Tubes			
0.00	0.41	0.44	0.62	—	0.60
0.05	—	—	—	—	0.33
0.33	—	—	—	0.36	—

The final volume (Table II) of the suspension was thus reduced to 8.9 and 8.0 cc. for TiO_2-I and TiO_2-II respectively in the absence of oleic acid, and to 3.9 and 3.1 cc. for an initial oleic acid concentration of 0.0111 moles per kg. of benzene.

Thus, when the particles are covered with a monomolecular film of oleic acid, the final volume of the suspension becomes in this way as small as or smaller than the volume of the dry powder. After the suspensions which contained oleic acid had settled to such a compact mass, it was very difficult to cause a resuspension of the powder by shaking, and to this extent the behavior is analogous to that known as the hard-settling of paints. For example, 45 minutes of vigorous shaking by hand was necessary to resuspend the powder in one of these tubes.
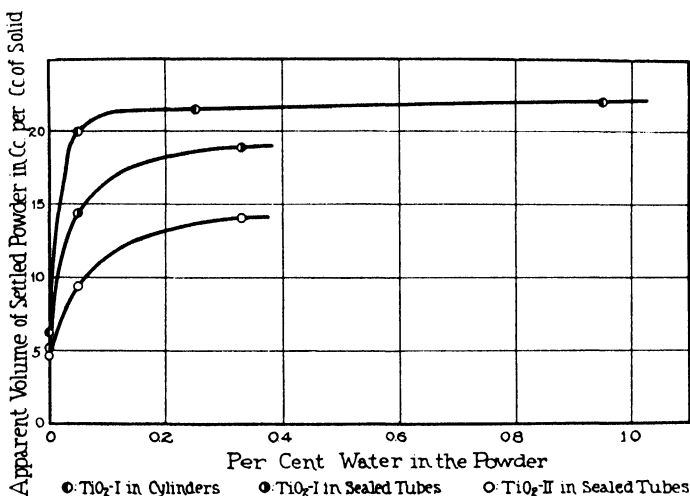
FIG. 3

Variation of Extent of Settling with Water Content of Powder

7. The Effect of Water

The results of certain experiments on the adsorption of oleic acid by titanic oxide have been given, but an important additional result obtained was that powder with a content of 0.05 per cent water, in the form of an adsorbed layer, adsorbs only about one-half as much oleic acid as the dry powder. Since the oleic acid film is very effective in producing settling of the suspension in benzene, it seemed important to determine the relation between the water content and the settling.

The results of the experiments are shown in Fig. 3. Powders which have settled completely to about 5 cu. cm. per cu. cm. of solid, are found to settle less and less as the water content is increased.

The data are summarized in Table I. In the first series (A) of experiments the presence of 0.33 per cent of water with the powder was sufficient to entirely

prevent the settling due to oleic acid, while in the second and third series the presence of this amount of water was found to overcome largely but not entirely the effect of the acid.

8.   Texture of the Suspension

As has been shown, titanic oxide in dry benzene gives a suspension with a large specific volume, about 21 cu. cm. per cu. cm. of solid. The suspension, after settling, is found to exhibit a coarse structure, sometimes with cavities one mm. or more in diameter. Such a suspension is often described as "flocculated." If the suspension is shaken in the sealed tube, the walls of the glass become coated with a flocculated coating, which does not completely cover the glass, and which may be easily detached. Very little of the powder adheres to that part of the glass which is under the liquid.

An interesting phenomenon was observed with such tubes when the powder and dry benzene only were present. If such a sealed tube is shaken vigorously, it gives a spark over a gap of about 3 mm. if the glass is brought near the hand. Tubes in which oleic acid is also present were not found to exhibit this phenomenon, though it is possible that the glass becomes charged to a lesser extent.

When the suspension contains enough oleic acid to produce the maximum settling, the texture is very uniform and fine, and the suspension may be said to be deflocculated. With such suspensions the deposit on the glass is much more fine and more adherent.

If water is added, the suspension, after it is shaken, is found to be flocculated, and the structure of the suspension, with 0.33% of water to powder, is apparently the same as if neither oleic acid nor water were present.

9.   Rate of Settling as influenced by the Composition of the Liquid

The rate of settling of the powder in benzene solutions which contain different amounts of oleic acid and of water is exhibited in Fig. 4. A striking feature of these curves is that in pure benzene the powder settles the most rapidly at first but settles least in 24 hours. If only oleic acid is added the rate of settling is often practically constant for an hour, and increases with increasing acid concentration up to a concentration of acid (about 0.01 m.) which gives a complete monomolecular film.

A peculiar relation is shown by curves b and c. The system is the same for both of these (0.0016 moles of oleic acid per kg. of benzene). Both settle at the same rate for three minutes and to the same extent in 24 hours. However, at the end of 3 minutes suspension c began to settle much more rapidly than b and departed very widely from the linear course of the latter.

Fig. 5 illustrates the behavior of a suspension in a tube which was called the "clock-tube," since it behaved with such regularity as to give a moderately accurate measure of an interval of time, four minutes in length, and also a shorter interval of about three minutes. The titanic oxide contained 0.33 per cent of water, and was suspended in a solution which contained 0.035 moles of oleic acid per kg. of benzene. For four minutes the powder settled
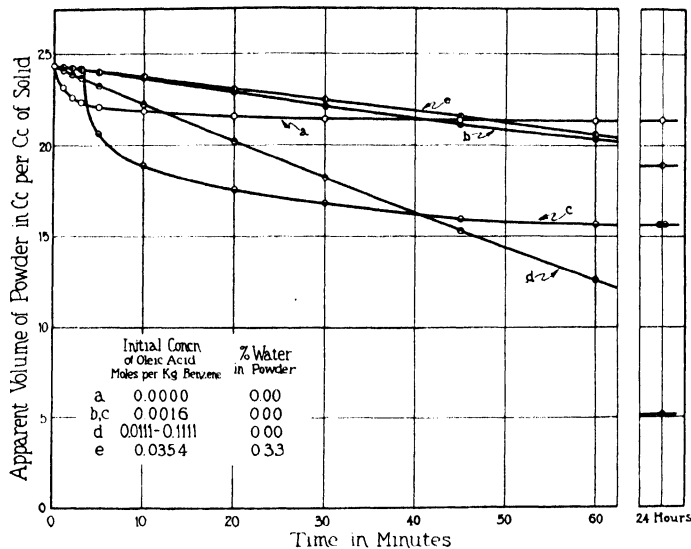
FIG. 4

Typical Settling Curves for Titanic Oxide

with extreme slowness (from 24.4 to 24.2 cu. cm.) at the top, and at the end of this period it fell with considerable rapidity from 24.2 cu. cm. at 4 minutes to 17 cu. cm. at 5 minutes and to 15 cu. cm. at 6 minutes, while in 60 minutes it fell only to 14 cu. cm. This procedure was repeated many times, after the tube was shaken.
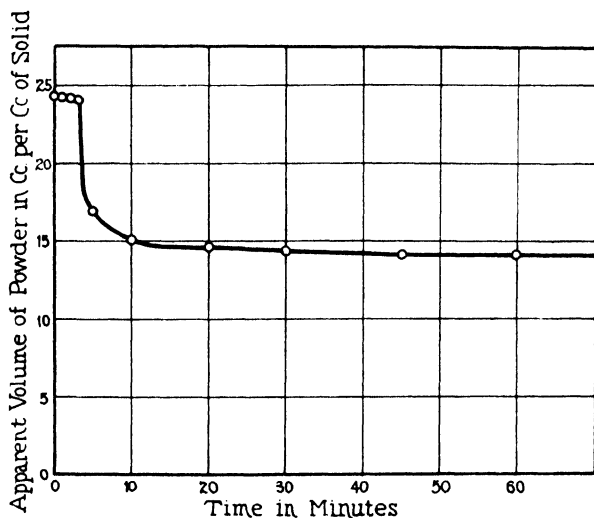
FIG. 5

Abnormal Settling Curve. Titanic Oxide plus 0.33% of Water, Solution of 0.035 Moles Oleic Acid per Kg

At the beginning of the period the suspension appeared to be uniform (not flocculated), and this condition persisted for 4 minutes near the top of the cylinder, but only 3 minutes at the bottom. At the end of 3 minutes the suspension seemed to begin to settle suddenly and rapidly near the bottom of the tube. This settling drew the powder mostly away from a region about 2 cm. above the bottom of the tube. Then powder fell rapidly into this vacant space from just above, and by the continuation of this process the region almost free from powder moved rapidly up the tube.

The effect of n-butyric, n-heptylic, stearic and oleic acid on the rate of settling of graphite, barium sulphate, and silica gel in benzene, has been studied by Rehbinder and his collaborators.[1] Their conclusions agree to a certain extent with those of the present paper, but a comparison is difficult since they studied the settling for about a one minute period only.

10. Orientation of the Molecules at the Interface Solid-Liquid

The values of the energy of immersion of oxides, such as titanic oxide, stannic oxide, silicon dioxide, and zinc oxide, indicate that in suspensions in benzene the carboxyl group of the acid is in all cases oriented toward the surface of the solid oxide (Fig. 6).

Liquid

Solid
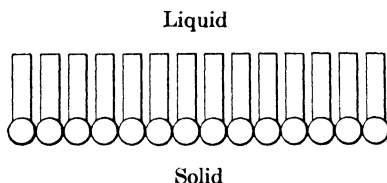
Fig. 6
Orientation of an Acid at the Surface of an Oxide

11. Discussion

It is often considered that the settling of powders in liquids and other related characteristics of the suspensions, are a simple function of the "wettability" of the powder by the liquid, but this is not true. Thus, it has been seen that dry titanic oxide in dry benzene settles only slightly. If oleic acid is present the heat of immersion is much higher, and the powder settles much more. However, the presence of small amounts of water in addition to the oleic acid may altogether prevent any additional settling due to the acid. The energy of immersion of the solid oxide in water, or in benzene which contains water, is even higher than the similar values with oleic acid. Thus the correlation of extent of settling with energy of wetting is not a simple one.

It has been seen, however, that the presence of a monomolecular film of oleic acid on the grains of powder greatly increases the amount of settling, and causes deflocculation. The effect might be ascribed to a lubricating action of

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[1] Rehbinder, Lagutkina, and Wenström: Z. physik. Chem., 146 A, 63 (1930).

the monomolecular film which does not allow one particle of powder to adhere to another. This behavior may be assumed to be due to the electrical relations at the interface solid-liquid. Thus the particles may be considered as more highly charged when oleic acid is present than when it is absent, but no evidence in favor of this conclusion has been obtained. The energy of adhesion and of cohesion may be involved as well. More work is being done on the various factors which affect the flocculation.

The writers wish to thank L. W. Ryan, Director of Research, Titanium Pigment Co., Inc., for many useful suggestions.

12. Summary

1. A monomolecular film of oleic acid on the surface of a fine powder suspended in a very dry non-polar liquid, is found to deflocculate the powder, and to cause it to settle to one-fourth the volume it would occupy if no oleic acid were present. This effect is produced by a monomolecular film of oleic acid even if it is not quite a condensed film. Thus the final volume occupied by 1 cu. cm. of titanic oxide in its flocculated suspension in pure and very dry benzene is 20 cu. cm., but this is reduced to 5 cu. cm. by a monomolecular film of oleic acid on each grain of powder.

2. Vibration of the tubes which contained the suspensions greatly reduced the above volumes to about 8 and 3 cu. cm. respectively. Thus the reduction in volume did not annul the great effect of the film of oleic acid.

3. The addition of very small amounts of water to the solution of oleic acid in benzene was found either to destroy entirely or else to remove partly the effect of the oleic acid in deflocculating the solution and causing settling to a small volume. Thus water caused the flocculation to reappear. The final volume of 1 cu. cm. of titanic oxide powder in dry benzene was found to be 20.3 cu. cm., which was reduced to 6.5 cu. cm. by an initial concentration of 0.00827 moles of oleic acid per kg. of benzene. The presence of 0.05% of water in the titanic oxide increased this volume of the suspension to 20.8 cu. cm. or slightly more than the volume when no oleic was present. Thus water partly replaces the oleic acid in the adsorbed film at the solid-liquid interface.

4. An adsorption method for the determination of the area of the surface of a fine powder is described. The powder is immersed in extremely dry benzene to which small varying amounts of oleic acid are added. The maximum adsorption is found to correspond to a monomolecular film of the acid. It is assumed that the area occupied per molecule of oleic acid in this saturated film is the same as in a condensed film of oleic acid on water, that is 20 sq. Å., or 20×10^{-16} sq. cm. The area thus determined has been found to agree as well as could be expected with the results of a microscopic determination.

5. It is shown that the extent of the flocculation and of the settling is not, as is sometimes supposed, a simple function of the "wettability" of the powder by the liquid. Thus titanium oxide exhibits a high energy of immersion with

both oleic acid and water and a low energy with benzene, yet oleic acid in benzene deflocculates the suspension, while if water is added, the suspension becomes re-flocculated.

6. The composition of the organic liquid in which the powder is suspended has a remarkable influence upon the rate of settling of the suspension. In general the titanic oxide settles most in the end when it settles least rapidly initially.

7. In general the volume of the suspension, when it settles without vibration, varies inversely with the extent of the flocculation.

University of Chicago,
July 27, 1931.

MONOMOLECULAR FILMS.* THE LIQUID-LIQUID INTERFACE AND THE STABILITY OF EMULSIONS[1]

EARL K. FISCHER[2] AND WILLIAM D. HARKINS

I. Introduction

Membranes play an extremely important part in both animal and plant physiology and in all phenomena characteristic of life. It is the purpose of the series of researches, of which this is the first, to determine something more than is now known concerning membranes, particularly of the organic type.

From the physical standpoint a membrane is a thin layer which has commonly two surfaces, or in more general terms, two interfaces between the adjacent phases. These may act to adsorb films. The layer often has the structure of a gel and is sometimes considered to be built up from micellae, which are supposed to adsorb various substances upon their surfaces.

The nature of the interfacial film in oil-in-water emulsions has been the subject of considerable theoretical speculation, since such emulsions offer, through their relatively simple constitution, a means for the determination of the thickness of interfacial films, which cannot at present be determined directly for the films present in such complicated systems as those in which membranes exist. Harkins and Beeman[3] point out that in this connection several topics deserve a much more thorough investigation. These are: (1) the number of molecules of emulsifying agent per unit area of the oil-water interface, (2) the stability of emulsions and the effect of aging, and (3) the oriented wedge theory of emulsions.

Therefore in the study of membranes it seems to be of fundamental importance to determine the thickness of adsorbed interfacial films. According to McBain[4] substances soluble in one of the phases adjacent to the interface give polymolecular films. While this is on the whole contrary to the prevalent opinion, it seemed essential to determine by as direct a method as possible what the thickness of the film actually is. It was therefore decided to investigate still further the thickness of the soap film between the phases oil and water, such as are present in an emulsion.

The first somewhat direct values for the thickness of such a soap film were obtained by Griffin.[5] Kerosene was emulsified in aqueous soap solutions and

the apparent area per molecule was calculated from the interfacial area and the amount of soap adsorbed as determined analytically. The area for the sodium oleate molecule was determined as 48 sq. Å. This is considerably higher than the area for the fatty acid in a condensed monomolecular film, ca. 20 sq. Å.[6] At about the same time van der Meulen and Rieman[7] studied emulsions of oil stabilized with potassium chaulmoograte and found areas for the soap molecule which corresponded with a monomolecular film within the limits of experimental error.

In the work of Griffin and that of van der Meulen and Rieman the calculation of the interfacial area was based upon the measurement of such a small number of drops that no conclusive evidence as to the molecular area was obtained. A marked improvement in the method was introduced by Harkins and Beeman, who made careful determinations, involving thousands of sizes of oil droplets, of the distribution of sizes of the oil particles in the emulsion.

In the present paper are reported results obtained by a direct microscopic count of the size distribution of oil particles to determine the specific interfacial area together with analyses to determine the amount of emulsifying agent removed. Data are also given which indicate that the soap film is labile and changes with aging of the emulsion. The results indicate that a monomolecular layer of soap molecules forms at the interface.

II. Experimental Methods

1. *Projection Equipment.*—The microscopic equipment consisted of a microscope fitted with a 61 ×, 3 mm. oil immersion apochromatic objective, N. A. 1.40; a Zeiss "Homal" projection lens; a 2 inch glass prism; and a 12 mm. aplanatic condenser. The microscope was mounted on a steel base in conjunction with a clock feed arc lamp operating at 5 amperes on 110 volts direct current. A water cell was used to filter the light.

The screen, size 4 feet square, was painted with a flat white titanium oxide paint. Calibration of the optical equipment was made with an ocular micrometer slide. Magnification was such that an image of 8 mm. diameter on the screen corresponded to a particle 1 micron in diameter.

The cell was designed earlier by Harkins to reduce the tendency of the particles to segregate according to sizes. A microscope slide of thin glass contained a cell 4 mm. in diameter, the base of which is divided into minute squares, and with a depth of 0.010 mm. The cell was surrounded by a circular depression 0.5 mm. deep and 3 mm. wide. Two small grooves leading from this depression allowed any excess solution to flow off when the cover glass was put in place.

2. *Materials.* Oils.—Most of the emulsions studied were prepared from "Finol," a highly refined paraffin oil sold by the Standard Oil Co. of Indians. "Stanolax," a similar oil, but of higher viscosity, was also used.

[6] Adam: Proc. Roy. Soc., **101A**, 516 (1922).

[7] J. Am. Chem. Soc., **46**, 876 (1924).

The specific gravity of Finol is 0.885 and of Stanolax, 0.889 at 15.6°C. The viscosities of the oils are as follows: Finol, 0.170 poise; Stanolax, 0.524 poise at 37.8°C.

Soap.—Sodium oleate was prepared from oleic acid from two sources. In one series of preparations, U. S. P. oleic acid was purified through the lead and barium salt treatment[8]; in a later series Eimer and Amend C. P. oleic acid was used directly. The soaps were prepared from sodium ethoxide and oleic acid as described by Harkins and Beeman, except that from three to four recrystallizations from alcohol were made before the soap was used.

3. *Preparation of the Emulsions.*—A fresh soap solution was stirred with the oil by means of an Arnold drink mixer or a motor-driven egg beater. For emulsions prepared from comparatively dilute solutions, it was found advisable to place the soap solution in the stirring cup and to add the oil in a thin stream while stirring. The time of stirring was usually ten minutes. When a large quantity of a given emulsion was prepared it was stirred in small batches; these were combined in a large beaker, and the whole was then beaten with the motor-driven egg-beater. The resulting emulsion was placed in separatory funnels and the stoppers were sealed with paraffin. For the analyses it was convenient to have about 100 cc. of the aqueous layer. Accordingly most emulsions were made with 150-200 cc. of the oil and soap solution in equal proportions.

4. *Sampling and Measuring the Particle Sizes.*—After the emulsion had stood for several hours a partial separation of the emulsified oil and the excess soap solution took place. The lower aqueous layer of soap solution was drawn off, leaving the cream in the separatory funnel. This layer of emulsified oil retained from 25 to 40% of the aqueous solution depending on the time the emulsion had stood and the relative sizes of the particles. Emulsions with large oil particles cream rapidly. The emulsion was mixed by rotating the separatory funnel, avoiding any violent agitation. A portion of this thoroughly mixed cream was removed with a pipette and diluted approximately 1000 times with a dilute soap solution. Water was not used for the dilution, for that tended to dissolve the stabilizing soap layer and the emulsion broke while it was on the microscope slide.

A drop of the diluted emulsion was placed in the cell and covered with a thin cover glass. Finol was used for contact between the oil immersion objective and the cover glass. Measurements were made on every drop in the field. The slide was shifted by means of the mechanical stage so that a succession of independent areas were examined. The sizes were recorded with a typewriter or by an assistant who tallied the count. Four to five separate dilutions were made in each experiment. Measurements on moving spheres are difficult to make, for the size appears to change with the focus of the microscope, position of the arc carbons, and fatigue of the eyes.

5. *Analyses.*—The soap solutions were analysed as follows: A portion was pipetted into a separatory funnel, and N sulfuric acid was added in quan-

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[8] Lawrence: "Soap Films," 134 (1929); Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats, and Waxes," 1, 140 (1909).

tity sufficient to provide an excess of acid over that necessary to neutralize the free alkali and to liberate the fatty acid from the soap. The aqueous mixture was extracted five times with C. P. ether, and the combined ether extracts were washed three to four times with distilled water until the wash water was neutral to litmus. The ether was evaporated nearly to the appearance of the oily fatty acid, neutral alcohol was added, and the oleic acid was titrated with standard alkali from a weight burette, using phenolphthalein as indicator. The original soap preparation was analysed at the same time that the analysis was made on the soap which had separated from the emulsion. The difference between the two titrations represents the amount of soap in the interface.

Sodium was determined both as the sulfate[9] and as the complex uranyl-zinc-acetate.[10]

III. Results and Discussion

1. *Calculation of the Interfacial Area.*—The diameter and number of oil spheres give a basis for the calculation of the total area and volume represented by each size group. From these totals the specific interfacial area, or the area of interface in cm.^{2} per cc. of emulsion is given by the following relation,

$$\text{Specific Interfacial Area (cm.}^2 \text{ per cc.)} = \frac{\text{Total Area (cm.}^2)}{\text{Total Volume (cc.)}}$$

The analytical data give the number of moles of soap removed during emulsification, calculated both from the sodium and the oleic acid determinations. The apparent area of the soap molecule, if the ratio of oil to soap solution in the emulsio is 1:1, is given by

$$\frac{\text{Area of Soap}}{\text{Molecule}} = \frac{\text{Specific Interfacial Area}}{\text{Number of Moles of Soap removed per Cu. Cm.} \times N}$$

Where N is the Avogadro constant, 6.062×10^{23}.

The number of moles of soap removed is determined in the aqueous phase, and what is desired is the number of molecules calculated as if removed from the oil phase, so in general the extra factor V_o/V_a, or ratio of volume of oil to aqueous phase is used on the right side of the equation.

2. *Particle Size Distribution.*—In the determination of the distribution of particle size in each emulsion at least 1000 droplets, and commonly from 2000 to 3000, were measured. Typical curves which show the relation of the diameter of the particles to the percentage number of particles which have that diameter, are shown in Fig. 1. In most of the emulsions of a paraffin oil the maximum number of particles corresponds to a diameter of about 1 micron. With benzene the maximum occurs at a smaller diameter.

In Fig. 2 the area per cc. is plotted against particle size. It will be observed that the greatest contribution to the area is given by particles between 6 and 7 microns in the Finol emulsions and 1 and 2 microns in the benzene emulsions. Table I is a total of a large number of experiments on emulsions prepared with Finol, but disregarding the soap concentration.

[9] Scott: "Standard Methods of Chemical Analysis," 1, 409 (1925).
[10] Barber and Kolthoff: J. Am. Chem. Soc., 50, 1625 (1928).
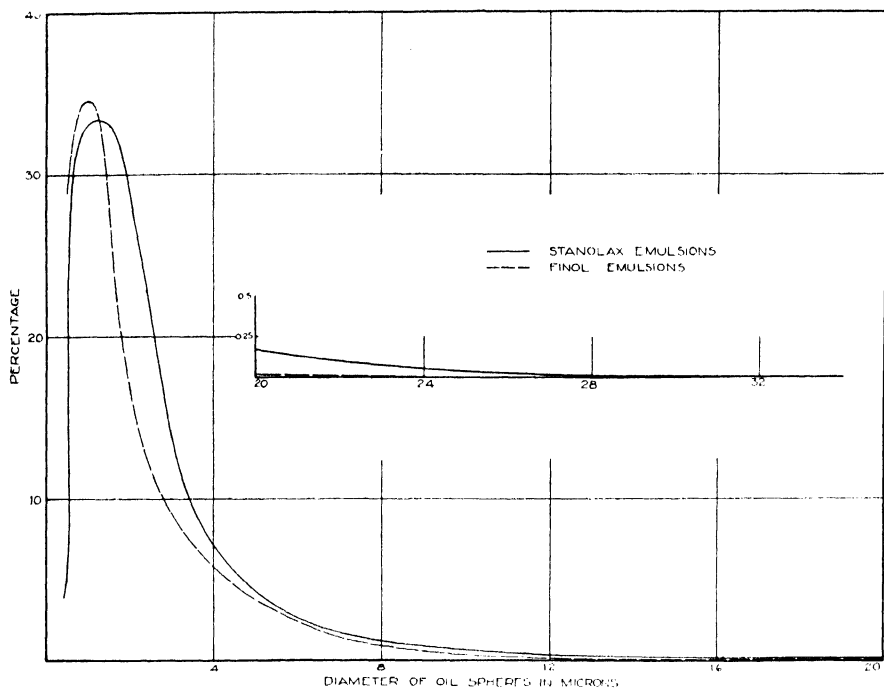
FIG. 1

Size Distribution of Oil Particles in Finol (50,000 droplets) and Stanolax Emulsions
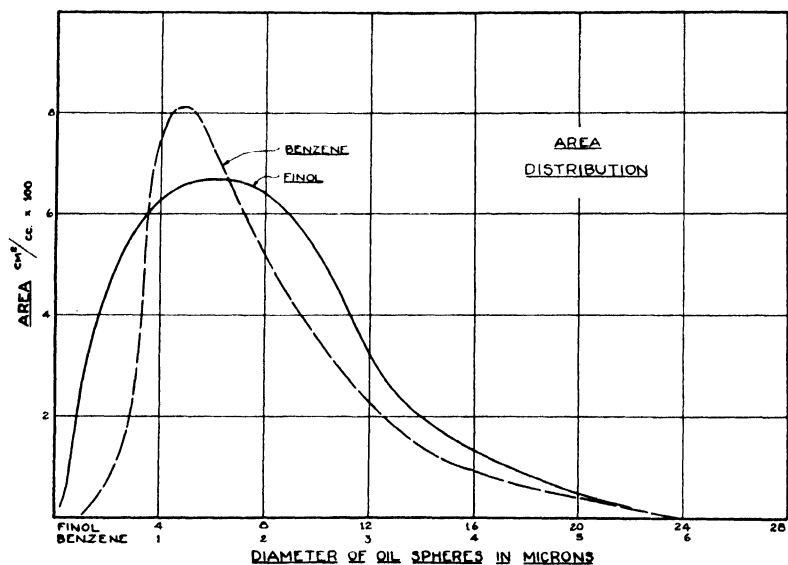
FIG. 2

Distribution of Area with Diameter in Emulsions of a Light Paraffin Oil
(50,000 droplets), and of Benzene, in Water

TABLE I

Combined Size Distribution Determinations of Finol Emulsions

Size in microns	Number counted	%	Number from smooth curve	%	Area cm.² $\times 10^5$	Volume cc. $\times 10^{10}$	Area per unit volume cm.²/cc. $\times 10^{-1}$
0.75	7518	15.204	7518	15.204	13.3	16	5.85
1	19511	39.459	19511	39.459	61.2	102	26.93
2	8259	16.703	8259	16.703	104.0	379	45.74
3	4897	9.904	4588	9.279	129.8	646	57.07
4	2569	5.195	2876	5.818	144.6	963	63.59
5	1981	4.006	1915	3.873	150.0	1254	65.94
6	1193	2.413	1352	2.734	152.4	1524	67.00
7	995	2.012	996	2.014	153.3	1792	67.42
8	828	1.675	730	1.476	146.7	1956	64.50
9	442	0.895	530	1.072	134.6	2023	59.17
10	534	1.080	383	0.775	120.2	2005	52.86
11	145	0.293	265	0.536	100.7	1846	44.26
12	144	0.291	160	0.324	72.3	1447	31.79
13	106	0.214	106	0.214	56.2	1219	24.74
14	130	0.264	78	0.158	48.0	1120	21.12
15	66	0.133	60	0.121	42.4	1060	18.64
16	52	0.105	44	0.089	35.3	943	15.55
17	26	0.054	30	0.061	27.2	771	11.97
18	21	0.042	20	0.040	20.3	610	8.95
19	7	0.014	12	0.024	13.6	430	5.98
20	19	0.038	6	0.012	7.5	251	3.31
21	0	0.000	3.5	0.007	4.7	169	2.08
22	2	0.004	2.0	0.004	3.0	111	1.33
23	0	0.000	1.1	0.002	1.8	70	0.80
24	1	0.002	0.4	0.001	0.7	28	0.31
	49,446	100.000	49,446.0	100.000	1,743.8	22,735	766.90

Specific Area (per cu. cm. oil) = 7670 sq. cm.

For the purpose of this work fairly stable emulsions were required. Those prepared with soap solutions of a concentration less than 0.006 M were found unsuitable, for on standing the oil gradually separated as a clear layer above the cream. It should be remarked, however, that the initial soap concentration gives very little indication of the lower limit of the soap concentration which is necessary for a stable emulsion. The amount of soap removed is dependent on the interfacial area, in consequence of which the final soap concentration is evidently of much greater significance.

Sodium hydroxide was added to most of the emulsions to repress the hydrolysis of the soap with a concomitant liberation of the fatty acid, which is soluble in the oil phase. The effect of excess alkali on the particle size distribution is very slight.

3. *Area Occupied by Sodium Oleate Molecule.*—The experimental methods employed in this investigation were essentially statistical and subject to several errors incident to such methods. It was found possible, however, to check the calculated interfacial area within 5% when disturbing factors did not enter.

This is of about the order of accuracy usually obtained in experiments on insoluble films with the film balance.

The area per molecule of soap in the interfacial film is shown by column 7 of Table II, to lie in general between 24 and 38 sq. Å. In the experiments the *final* concentration of the soap in the aqueous phase, at the time of the separation of the emulsion, varied from 0.0025 to 0.112 moles per liter. Since, as has already been stated, the area per molecule in a condensed monomolecular film of oleic acid at zero compression is about 20.5 sq. Å., it is seen that these areas correspond to somewhat expanded monomolecular film of oleic acid. However, the presence of electrostatically bound sodium ions instead of the more closely bound hydrogen of the acid, undoubtedly has an effect on the area, but does not change the monomolecular character of the film. More concerning this effect will be presented in the next section.

<div align="center">TABLE II</div>

Molecular Areas for the Soap at the Interfacial Film in Oil-in-Water Emulsions

Emulsion Number	Age of Emulsion in hours	Specific Interfacial Area Cm² per cc. $\times 10^{-3}$	Molarity of Equilibrium Soap	Molarity of Initial Soap	Normality of Sodium Hydroxide	Area of Sodium Oleate Molecule from Oleic Acid Analysis Sq. Å	Area of Sodium Oleate Molecule from Sodium Analysis Sq. Å
47				0.004	0.0004	Emulsion	Unstable
48	18	11.2	0.0025	0.0066	0.0002	44.5	44.6
33[1]	138	6.08	0.0043	0.0100	0.004	26.1	
46[2]	78	11.9	0.0047	0.0083	0.0002	18.2	
34[5]	720	5.58	0.0053	0.0114	0.004	30.2	29.6
32	168	6.00	0.0059	0.0100	0.004	24.2	26.1
39	3[3]	5.43	0.00718	0.01040	0.002	27.8	28.9
40	48	6.64	0.00634	0.01030	0.002	27.6	29.6
43[4]	144	11.2	0.00920	0.01800	0.0018	38.2	32.5
36[5]	190	6.17	0.0199	0.0254	0.0024	37.4	46.0
23	72	9.96	0.0341	0.0390	0.0013	33.6	38.8
29	36	10.8	0.0655	0.0710	0.025	32.4	25.2
42	3[3]	12.9	0.112	0.120	0.020	27.0	26.4

[1] Ratio of oil to soap solution, 3:2.
[2] Ratio of oil to soap solution, 1:3.
[3] Separated by centrifuging three hours.
[4] Ratio of oil to soap solution, 1.82:1.
[5] Ratio of oil to soap solution, 2:1.

The molecular area for sodium oleate in two emulsions, to which no sodium hydroxide or other base had been added, of ages 3 and 120 hours, is given as 29 and 27 sq. Å. in column 7 of Table III. The apparent areas in column 6 are listed only for comparison. The difference between the values in the two columns represents oleic acid which has been produced by hydrolysis and which is dissolved in the oil droplets, but is in the calculation considered as in the film. The value 11.7 for emulsion 50D would give the idea that the film is two molecules thick to anyone who does not take the hydrolysis into account. However, results obtained with entirely similar emulsions indicate that it is monomolecular.

TABLE III

Molecular Areas for the Soap at the Interfacial Film in Oil-in-Water Emulsions.   (No excess Alkali present in Soap Solutions)

Emulsion Number	Age of Emulsion in Hours	Specific Interfacial Area. Cm² per cc. $\times 10^{-3}$	Molarity of Equilibrium Soap	Molarity of Initial Soap	Apparent[2] Area of Sodium Oleate Molecule from Oleic Acid Analysis Sq. Å	Area of Sodium Oleate Molecule from Sodium Analysis Sq. Å
37	3[1]	7.23	0.0102	0.0154	23.0	29.0
50A	120	8.30	0.0125	0.0204	17.3	27.0
50D	1460	6.28	0.0114	0.0204	11.7	

[1] Separated by centrifuging three hours.

[2] On account of hydrolysis the values listed in this column are entirely fictitious, since they have been calculated by including oleic acid dissolved in the oil, as well as that in the film. The molecular areas are given in the last column.

4.   *Decrease in Molecular Area with the Age of the Emulsion.*—If oil is emulsified in a *dilute* soap solution it is often found to exhibit a somewhat large molecular area, of the order of 40 to 50 sq. Å., for the soap in the interfacial film.

In such cases it was discovered by Harkins and Beeman that the mean size of the oil droplets in the emulsion increases with its age. Their data indicate that concomitantly with this decrease of size and the corresponding decrease in interfacial area, *there is a decrease in the molecular area of the soap.* However, they did not determine the extent of this decrease, although they developed an hypothesis, given later, concerning it.

In order to determine the decrease in molecular area, the writers have carried out a very carefully conducted experiment on the aging of an emulsion produced by 0.02 molar sodium oleate as an emulsifying agent, in the presence of 0.004 molar sodium hydroxide, used to repress hydrolysis.

Fig. 3 shows that the specific interfacial area for this emulsion falls rapidly as follows, where the values are given in 10^3 sq. cm.: 9 at the end of 3 hours, 7 at 18 hours, 6 at 50 hours, 5.5 at 648 hours, and 5.25 at 2668 hours (111 days).
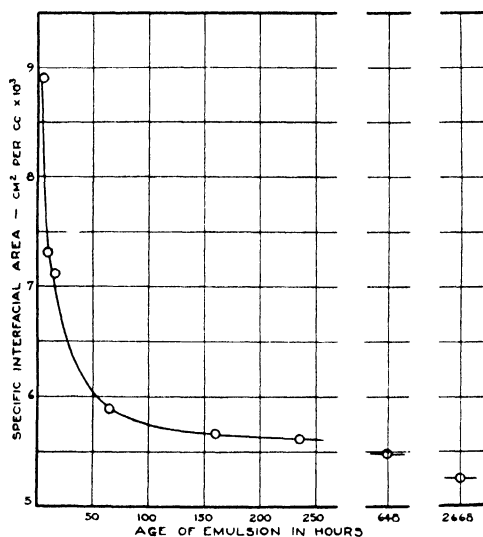
FIG. 3

Decrease in Interfacial Area with the Age of an Emulsion in
which the Emulsifying Agent was 0.02 molar Sodium Oleate

This reduction of area is not brought about by any separation of the oil in
bulk, but by a disappearance of small droplets by coalescence with larger ones,
and the resultant growth of the larger drops.   The change in the distribution
of sizes is given in Fig. 4, which represents a period of 3 months.   Many more
curves were determined, but their inclusion in a single figure makes it difficult
to follow.   At the end of 5 hours after the preparation the peak in the curve is
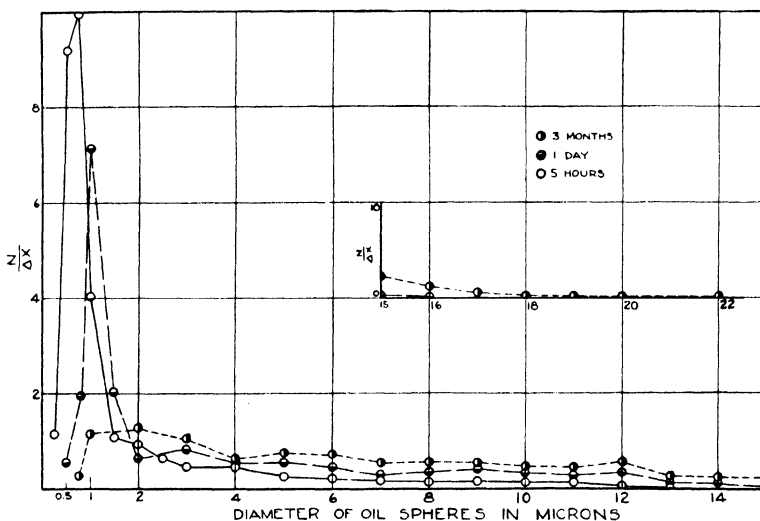
FIG. 4

Change in the Distribution of Diameters in an Emulsion with Its Age

at a diameter of 0.75 micron, and a height 10, at the end of 1 day at 1 micron and a height 7.2, and at the end of 3 months the curve is greatly flattened, with the maximum number of particles at 1 and 2 microns, and a maximum height of 1.2. The largest drops at 5 hours have a diameter of 13, at 1 day 16 and at 3 months 22 microns. The other six curves, which have not been included, illustrate very beautifully the gradual decrease in the height of the peak, its shift to the right, and the flattening of the curve. Similar curves, with a more rapid change were obtained by the use of more dilute soaps in the work of Harkins and Beeman.
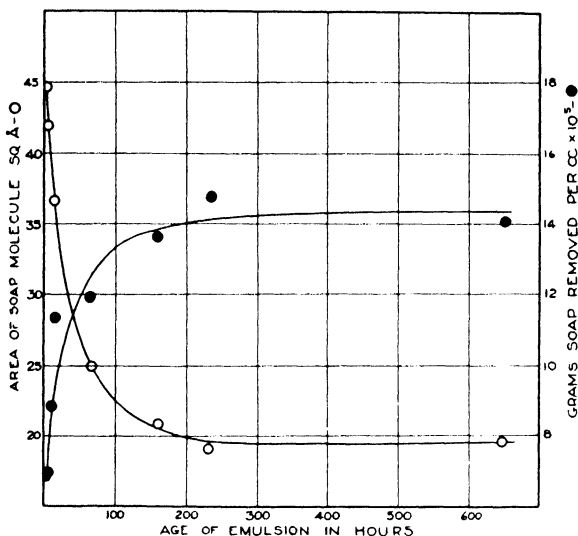
FIG. 5

[Decrease of the Molecular Area of Sodium Oleate in Emulsion with Its Age

A large amount of this emulsion was prepared, and stored in a considerable number of large separating funnels. The first sample used for a determination of the distribution of sizes and for analysis, was centrifuged at the end of 3 hours. The other samples were allowed to cream under the influence of gravitation. The samples which were kept for longer periods than the time necessary to separate the emulsion in this way, were mixed with extreme gentleness by rolling slowly by hand, in such a way as to prevent further emulsification. The mixing was essential to allow the film to come more closely into equilibrium with the aqueous phase.

The values listed in column 4 of Table IV show how the concentration of the aqueous soap solution decreases with time, to the extent of 14% in 10 days, and not at all in the succeeding 17 days.

The initial area per molecule of soap is 44.6 sq. Å. (Fig. 5 and Table IV). A decrease of 14% in the soap content of the aqueous phase does not add sufficient soap to the film to change this highly expanded to a condensed monomolecular film, in which this area is reduced to about 20 sq. Å. The pro-

duction of a condensed film is thus due to two factors: 1. A reduction in the soap concentration of the aqueous phase. 2. A decrease in the interfacial area.

The first of these is represented in Fig. 5 by the amount of soap removed per cu. cm. This amount increases for 10 days and then remains practically constant.

The decrease in the molecular area of the soap with the age of the emulsion is given in column 5 of Table 4 and in Fig. 5. The area decreases from 44.6 sq. Å. at the end of 3 hours, along a quite smooth curve to a constant minimum of about 19.6 sq. Å. at the end of 10 days. At the end of 27 days the area was the same, within the limits of accuracy.

TABLE IV

Effect of Age of Emulsion on the Calculated Molecular Area for the Soap at the Interfacial Film in Oil-in-Water Emulsions

(1) Emulsion Number	(2) Age of Emulsion in Hours	(3) Specific Interfacial Area Cm² per cc. $\times 10^{-3}$	(4) Molarity of Equilibrium Soap	(5) Area of Sodium Oleate Molecule from Oleic Acid Analysis Sq. Å	(6) Area of Sodium Oleate Molecule from Sodium Analysis. Unanyl-Zinc-Acetate Method. Sq. Å	(7) Area of Sodium Oleate Molecule from Sodium Analysis Sodium Sulfate Method. Sq. Å
54	3	6.08	0.01776	44.6		41.5
53	5	5.79	0.01772	41.9		31.5
(52)	10	7.31	(0.03708)	(41.3)	(41.0)	
51A	16	7.12	0.01628	31.6	25.8	27.7
51B	64	5.88	0.01611	24.9		
51C	160	5.66	0.01553	20.9		19.2
51D	236	5.61	0.01515	19.1	19.8	
51E	648	5.48	0.01538	19.6		

Initial concentration of sodium oleate, 0.02000 M., in all emulsions except No. 52 which was 0.04000 M.
Initial concentration of excess sodium hydroxide, 0.0040 N.

Thus this series of experiments confirms the point of view of Harkins and Beeman, when they say, concerning an emulsion in which there was at first a highly expanded monomolecular film: "Such an emulsion is not stable, and on standing the area of its interface decreases, and the area per molecule of soap in the film decreases, until the area becomes about that for a tightly packed (or condensed) monomolecular film."

In some cases, however, emulsions produced by sufficiently concentrated solutions of emulsifying agents, 0.1 molar soap or more concentrated, do not exhibit any considerable decrease of interfacial area with time: indeed in some instances emulsions have stood for years without any detectable change. For example two emulsions in which 0.1 molar sodium oleate was the emulsifying agent as determined by them in one of these emulsions, and that determined

by Miss Sophie Berkman four years later were in as close agreement as if the determinations had been made on two samples of the same emulsion by the same worker at the same time.   Thus if the interfacial soap film is initially a condensed monomolecular film, the tendency for the drops to grow in size by coalescence seems to be largely, and in some cases practically wholly, removed.

5.   *Additional Conclusions.*—The work already described proves definitely that: (1) the interfacial film which produces emulsification is not colloidal, and (2) it is not thicker than one molecule of the emulsifying agent, when the emulsifying agent is molecularly dispersed in its solution.

6.   Both the aqueous phase of the emulsions, after the separation of the cream, and the soap solutions from which the emulsions were prepared, have been investigated by the use of a Leitz slit ultra-microscope.   It seems probable from this work that the ultramicroscopic droplets of oil do not add appreciably to the total area of the oil-water interface.

A portion of the emulsion was centrifuged for five hours at high speed. The oil particles separated as a thick cream, leaving a slightly opalescent solution which contained few particles visible in the miscroscope. This aqueous layer was diluted and examined in the slit ultramicroscope.   The dilution was such that from two to five particles were present in the field at a given instant. The colloidal particles present in the original soap solution were counted in the same way and subtracted from the count which was made on the emulsion. Appropriate corrections were made for the decrease in the soap concentration during emulsification.   The volume of oil in the emulsions was determined by a modified Babcock test.   From these data the average particle diameter was calculated to be 0.22 micron.   Although this method at best gives only an approximate *average size*, the conclusion seems justified that the ultra-microscopic oil particles do not contribute largely to the area of the interface.   Any area which is of this type, of which account has not been taken in this work, would slightly increase the molecular areas given in the paper, and thus would increase the evidence that the films are truly monomolecular.

IV.   Summary

1.   One of the most important results of the work presented in this paper is to give definite evidence which shows the validity of the hypothesis presented earlier by Harkins and Beeman, that the stability of an emulsion increases in general as the emulsifying film changes from an expanded to a condensed monomolecular film.   Thus they say concerning an emulsion produced by a very dilute emulsifying agent: "Such an emulsion is not stable, and on standing the area of its interface decreases, and the area per molecule of soap in the film decreases, until the area becomes about that for a tightly packed monomolecular film."   It is shown that in addition, additional emulsifying agent is withdrawn from the solution and goes into the film, as the emulsion ages.   Thus in an emulsion produced by 0.02 molar soap the initial molecular area of soap in the film was 44.5 sq. Å., and this decreases gradually along a smooth curve with respect to time, until the area falls to about 20 sq. Å., at which value it remains constant.

2.   Certain emulsions produced by sufficiently concentrated soaps as emulsifying agents very rapidly produce a condensed monomolecular film at the interface.   Such emulsions are often stable over a period of years, without any appreciable decrease.

3.   A distribution curve is presented for the variation of the interfacial area with the diameter in emulsions of a paraffin oil in water, produced by sodium oleate as an emulsifying agent.   The curve gives the results of the measurement of about 5×10^4 droplets.   A similar curve for benzene, obtained from the measurement of a smaller number of droplets is given for comparison. The maximum area occurs at 6.3 microns diameter with the light paraffin oil, and at about 1.2 microns with benzene.

4.   The most important result of this work is that it definitely contradicts the idea that surface and interfacial films are several molecules thick in all cases in which the adsorbed substance is soluble in one of the phases.   Soap films in particular have been recently supposed to be polymolecular, but it is now shown by accurate work, that they are monomolecular, and either expanded or condensed.

The writers wish to thank Julius Stieglitz and the Chemical Foundation for assistance which has made this investigation possible.

George Herbert Jones Chemical Laboratory,
University of Chicago.

ELECTROKINETIC POTENTIALS. X.
THE EFFECT OF PARTICLE SIZE ON THE POTENTIAL*

BY HENRY B. BULL AND ROSS AIKEN GORTNER

Introduction

The present study was an outgrowth of an effort to obtain a standard material for the investigation of electrokinetic phenomena. Much of the work on electrokinetics has been done on ill-defined materials and it has been almost impossible for other workers to repeat each other's results with any degree of precision. It seemed desirable that the different methods for determining the electrokinetic potentials be checked against each other using the same standard material. Accordingly it was decided to use very pure quartz powder for this purpose. Investigation however showed that the situation was not simple because the electrokinetic potential on quartz particles depends upon particle size. Accordingly it was necessary to study the effect of particle size on the potential.

Mooney[1] reports a decrease in cataphoretic mobility of red oil, benzyl chloride, iodobenzene, tribromhydrine and dimethylaniline measured in distilled water as the particle size is decreased. He found the mobility to start decreasing with the decreasing particle size at about 150μ.

Abramson's and L. Michaelis'[2] work on the cataphoresis of protein-covered particles seems to indicate that with such particles the mobility is independent of the size.

Experimental

Five pounds of pure well-formed quartz crystals were ground† to pass a twenty-mesh sieve, digested with aqua regia for six hours, washed by decantation forty times with distilled water and ten times with conductivity water, sucked dry on a Büchner funnel, and then heated at 800°C. for 12 hours in a muffle furnace. This quartz was subsequently separated into nine portions by means of different mesh screens.

The only electrolyte solutions used in this investigation were 1.0×10^{-4} N and 2.0×10^{-4} N NaCl. The NaCl was the purest obtainable. It was dried at 400° before weighing for solution. The water used in making the solution was twice distilled and had a conductance of about 1.5×10^{-5} mhos. The volumetric apparatus was calibrated. The solutions were used the same day they were made.

[1] J. Phys. Chem., **35**, 331 (1931); Phys. Rev., (2) **23**, 396 (1924).

[2] J. Gen. Physiol., **12**, 587 (1929).

The streaming potential method was used for determining the electro-kinetic potential on the quartz. The apparatus was the same as that described by Bull and Gortner.[3] No constant temperature bath was employed but all the work was done in a room the temperature of which was $24.5 \pm 0.5°$.

The conductivity of the salt solution in contact with 4.6μ size quartz was determined in the streaming potential cell. The other conductivities reported are those of the solution in bulk. This is deemed permissible because it was found that the surface conductance of the quartz larger than 4.6μ was small enough so that surface conductance could be neglected. The bulk conductivi-
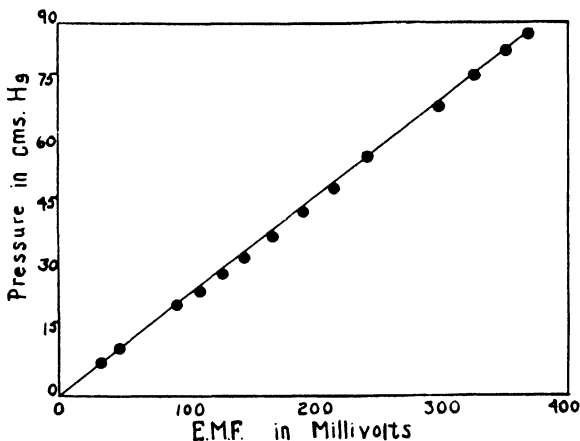
FIG. 1

Showing the relation between the streaming potential and the pressure, as experimentally determined in our apparatus using a cellulose dia-phragm and 1.0×10^{-4} N NaCl, as the liquid was being streamed thru the diaphragm

ties were determined using a conductivity cell described in detail by Washburn[4] for specific conductances in the range between 10^{-6} and 10^{-4} mhos. The resistance was determined with a Leeds and Northrup alternating current galvanometer. The cell constant was determined with both N/10 and N/100 KCl using the Kahlrausch values. Head phones tuned to 1000 cycles vibrations were used to determine the cell constant.

Since it was our original intention to obtain a standard material for electrokinetic work, and to check the streaming potential method against cataphoretic methods, using this material, we ground some of our quartz in an agate mortar until it remained in suspension when mixed with water. This quartz was packed in a diaphragm and its ζ-potential determined. The theory demands that there exist a linear relationship between the pressure applied on the liquid streaming thru the diaphragm and the electrical potential observed across the diaphragm as is shown in Fig. 1 for cellulose and an aqueous solution of 1.0×10^{-4} N NaCl.

[3] J. Phys. Chem., **35**, 309 (1931).
[4] J. Am. Chem. Soc., **38**, 2431 (1916).

To our surprise we found no such relationship with our quartz but instead, as is shown in Table I and Fig. 2, where the pressure is the abscissa and the streaming potential is the ordinate, we found a decreasing slope as we increased the pressure.

We found the same behavior to hold with 2.0×10^{-4} N NaCl and in later work used this concentration. Much time was spent in trying to determine the cause of this deviation from a straight line.

It is one of the fundamental requirements in the derivation of the streaming potential equation for calculating the zeta potential that Poiseuille's law for the flow of liquids thru capillaries be obeyed. It occurred to us that our difficulty might lie in the failure of this law of flow at higher pressures. This law states that the volume of liquid passing any cross section of a capillary in unit time is

$$V = \frac{\pi r^4}{8\eta} \frac{P_1 - P_2}{l}$$

where

η = coefficient of viscosity of the liquid flowing

r = radius of capillary

$P_1 - P_2$ = difference in pressure between the two ends of the capillary

l = length of capillary.
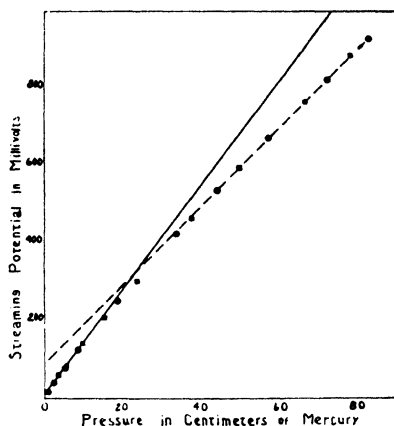
FIG. 2

Showing relation between pressure and the streaming potential with a heterogeneous mixture of quartz particles (sizes between .5µ and 36µ) and 1.0×10^{-4} N NaCl

TABLE I

Showing the Relationship between the Streaming Potential and Hydrostatic Pressure for a Quartz Diaphragm through which a 1.0×10^{-4} N Solution of NaCl was being streamed, the Quartz Particles being Non-uniform in Size.

Pressure (P) cm. Hg	Streaming Potential (H) mv.	H/P	Pressure (P) cm. Hg	Streaming Potential (H) mv.	H/P
			With decreasing pressure		
1.0	19.5	19.50	77.5	885.0	11.42
2.4	40.5	16.88	66.1	767.5	11.61
5.1	77.5	15.20	49.7	593.0	11.93
8.7	124.0	14.25	37.2	463.0	12.45
18.8	251.0	13.35	23.5	304.0	12.94
33.7	423.0	12.55	15.1	208.0	13.78
43.9	536.0	12.21	9.7	141.5	14.59
57.0	670.5	11.76	5.5	86.5	15.73
71.7	821.0	11.45	3.5	61.5	17.57
82.1	928.0	11.30	1.2	25.5	21.25

One test of this law is to determine the relation between the rate of flow of a liquid thru a capillary as a function of the pressure applied. Poiseuille's law demands that this function be linear and that the volume of the liquid in unit time per unit pressure be a constant. Accordingly the rate of flow thru a quartz diaphragm at different pressures was studied. The quartz diaphragm used was prepared from the same sample of quartz as that employed to obtain the data for Table I. The results shown in Table II were obtained. The data in Table II show that there is not a sufficient deviation from Poiseuille's law to explain the lack of linearality between the pressure and the streaming potential.

TABLE II

Testing Poiseuille's Law of Flow thru a Quartz Diaphragm made of a Heterogeneous Mixture of Quartz Particles (sizes between $.5\mu$ and 36μ in diameter) with an Aqueous Solution of 2.0×10^{-4} N NaCl.

Pressure (P) cm. Hg	Rate of Flow (V) grams of solution per min	V/P	Pressure (P) cm. Hg	Rate of Flow (V) grams of solution per min	V/P
8.0	.350	.0437	58.4	2.709	.0464
17.2	.786	.0457	67.0	3.126	.0466
26.3	1.190	.0452	75.9	3.462	.0456
37.4	1.750	.0468	82.3	3.950	.0480
48.0	2.260	.0461			

It was then decided to investigate the effect of particle size on the streaming potential. To this end that portion of the quartz powder which passed a 20 mesh sieve was further separated by sieving into nine portions. The particle size was assumed to be the arithmetic mean between the sieve size it was passed thru and that upon which it was retained. The three smallest sizes, i.e., 4.59μ, 31.1μ, and 74.91μ were determined by measurement of a number (75-100) of particles with a calibrated microscope and then taking the average of these measurements.

The 4.59μ size was packed in a diaphragm 1.1 cm. long and 2 cm. in diameter. The larger sized samples were packed in diaphragms 9.5 cm. long and 2 cm. in diameter. With this arrangement a convenient rate of liquid flow was obtained. Perforated gold electrodes were used at each end of the diaphragm. With the smaller quartz (98μ and below) a thin layer (about 1 mm.) of 214μ quartz was placed at each end of the diaphragm to keep the smaller quartz from washing thru the perforations in the electrodes. The diaphragms were washed with at least 500 cc. of the solution and were then allowed to remain 12 hours in contact with a portion of the electrolyte solution to be used. This portion was replaced by fresh solution before a measurement was attempted. The values reported and used in the graph of the results are the average of at least six or more readings.

Results

The results of the electrokinetic studies on the nine different particle sizes of the quartz are given in Table III thru Table XI, summarized in Table XII and graphed in Fig. 3.

TABLE III

2×10^{-4} N NaCl and 630μ Quartz

Pressure cm. in Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. Hg (P)	Streaming Potential in millivolts (H)	H/P
2.03	61.0	30.06	0.98	28.0	28.56
0.23	7.0	30.74	0.57	18.0	31.82
1.76	50.0	28.42	1.06	33.0	31.14
2.70	80.0	29.65	0.78	20.0	25.27
3.49	90.0	25.70		Average H/P =	29.04

TABLE IV

2×10^{-4} N NaCl and 330μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
0.71	20.0	28.29	1.23	35.0	28.42
1.33	40.0	30.06	0.90	25.0	27.61
.80	25.0	31.14		Average H/P =	29.10

TABLE V

2×10^{-4} N NaCl and 214μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
2.57	80.0	31.01	2.90	90.0	31.01
2.54	75.0	29.51	2.36	70.0	29.65
2.71	80.0	29.51	3.27	100.0	30.46
3.01	90.0	29.92		Average H/P =	30.15

TABLE VI

2×10^{-4} N NaCl and 163μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
2.93	90	30.76	3.31	100	30.23
3.08	90	29.21	2.81	80	28.49
3.28	95	28.97	2.84	80	28.19
				Average H/P =	29.31

TABLE VII

2×10^{-4} NaCl and 128μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.11	31.0	27.92	1.29	34.0	26.36
2.72	74.0	27.21	3.57	99.0	27.73
4.61	128.0	27.77	9.9	254.0	25.66
11.4	293.0	25.70	17.6	453.0	25.74
20.9	544.0	26.03	22.9	598.0	26.11
				Average H/P =	26.62

TABLE VIII

2×10^{-4} N NaCl and 98μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
3.86	104.0	26.94	19.5	465.0	23.85
9.1	223.0	24.51	34.2	830.0	24.27
21.9	545.0	24.89	1.61	38.0	23.60
31.4	775.0	24.68	3.57	84.0	23.53
1.53	40.0	26.14	8.6	188.0	21.86
4.08	103.0	25.25	18.7	423.0	22.62
10.6	250.0	23.58	34.0	780.0	22.94
				Average H/P =	24.19

TABLE IX

2×10^{-4} N NaCl and 74.9μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.90	40.0	21.05	4.06	97.0	23.89
3.97	89.0	22.42	9.60	216.0	22.50
9.60	210.0	21.88	19.50	453.0	23.23
18.70	431.0	23.05	27.60	635.0	23.01
28.40	665.0	23.42	37.30	850.0	22.79
1.42	35.5	25.00		Average H/P =	22.93

TABLE X

2×10^{-4} N NaCl and 31.1μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
1.41	30.0	21.28	29.70	595.0	20.03
3.75	78.0	20.80	40.30	818.0	20.30
9.20	177.0	19.24	52.50	1097.0	20.90
19.80	392.0	19.80	52.10	1099.0	21.09
29.80	604.0	20.27	4.50	85.0	18.89
40.40	826.0	20.45	9.00	166.5	18.50
51.10	1057.0	20.68	20.10	388.0	19.30
62.80	1310.0	20.86	29.00	567.0	19.55
1.33	30.0	22.56	40.10	792.0	19.75
3.77	77.0	20.42	50.60	1006.0	19.88
9.60	181.0	18.85	59.80	1191.0	19.92
19.60	381.0	19.44		Average H/P =	20.12

TABLE XI

2×10^{-4} N NaCl and 4.59μ Quartz

Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P	Pressure in cm. of Hg (P)	Streaming Potential in millivolts (H)	H/P
3.47	23.0	6.63	47.20	302.5	6.41
11.60	65.0	5.60	62.50	392.0	6.27
18.40	116.0	6.30	73.50	456.0	6.20
31.40	199.0	6.34		Average H/P =	6.25

TABLE XII

Summary of Electrokinetic Potentials at a Quartz-Aqueous 2.0×10^{-4} N NaCl Interface. Showing the Effect of Particle Size.

Particle diameter in μ	log μ	H/P	$\kappa_s \times 10^6$ mhos	$H\kappa_s/P$	log $H\kappa_s/P$
630	2.799	29.04	28.90	83.93	1.924
330	2.519	29.10	28.90	84.10	1.925
214	2.330	30.15	28.90	87.13	1.940
163	2.212	29.31	28.90	84.71	1.928
128	2.107	26.62	28.90	76.93	1.886
98	1.991	24.19	28.90	69.91	1.845
74.9	1.875	22.93	28.90	66.27	1.821
31.1	1.493	20.12	28.90	58.15	1.765
4.59	0.662	6.25	35.81	22.38	1.350

Discussion

It is our belief that the deviation from a linear relation between pressure and the streaming potential is due to the fact that the ζ-potential on the quartz particles is different for different size particles. This lack of linearality was observed only with a heterogeneous mixture of particle sizes. When the quartz was separated into its fractions of relatively uniform particle size a
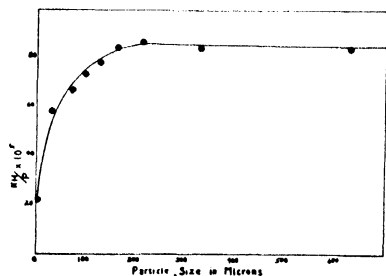
FIG. 3

Showing the relation between the electrokinetic potentials at a quartz-aqueous 2.0 × 10⁻⁴ N NaCl inter-face for different particle sizes
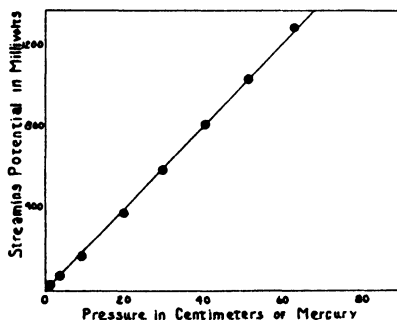
FIG. 4

Showing relation between pressure and electrokinetic potential for a homogeneous particle size. (Data from Table X. 2 × 10⁻⁴ N NaCl and 31.1 μ quartz).
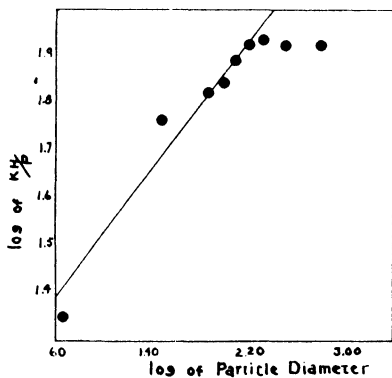
FIG. 5

Plot of log $H\kappa_s/P$ against log μ. The straight line is drawn on the assumption that $H\kappa_s/P$ varies as the cube root of μ

good straight line was obtained between pressure and the streaming potential as is demonstrated in Fig. 4 plotted from the data of Table X.

It seems probable that as the pressure is increased the smaller quartz particles are displaced into the places of maximum flow, thus protecting the larger particles and diminishing their importance in the picture, and, since it is the larger particles which have the higher potential, naturally the ratio between the streaming potential and pressure decreases, thus producing the effect shown in Fig. 2.

In Fig. 5 the log of the particle diameter is plotted as the abscissa against log $H\kappa_s/P$ as the ordinate.

From a particle size of 4.59μ to 214μ an approximate straight line is obtained whose slope is 1/3, which means that $H\kappa_s/P$ varies roughly as the cube root of the diameter of the particle. It is suggestive that as we decrease the particle size the ratio of edge length and number of corners to the surface area of the particles increases. Now there is reason to believe that, due to un-

satisfied valencies in the crystal lattice, more adsorption occurs at the edges and corners than on the flat surfaces[5] so that as we decrease the particle size of the quartz we should expect more adsorption per unit area, which would be equivalent to having a higher salt concentration at the interface which, in turn, would undoubtedly produce a lower electrokinetic potential and thus account for the fact that the smaller quartz particles were found to have a smaller electrokinetic potential.

Summary

1) Pure quartz crystals were ground to pass a 20 mesh sieve, thoroughly cleaned and separated into nine portions according to the particle size. Electrokinetic studies were conducted on this quartz in an aqueous solution of 0.20×10^{-3} N NaCl.

2) In a heterogeneous mixture of different size quartz particles, no linear relation was found between the pressure forcing the liquid thru the quartz diaphragm and the streaming potential. Poiseuille's law was found to hold with this quartz.

3) In a more homogeneous mixture of quartz particles a good linear relation was found between the pressure forcing the liquid thru the quartz diaphragm and the streaming potential.

4) Between a particle size of 4.59μ and 214μ the surface potential was found to increase roughly as the cube root of the diameter.

5) It is suggested that the lack of linearality between the streaming potential and the pressure in a heterogeneous mixture of particle sizes is due to the fact that the smaller particles have a smaller surface potential.

6) It is also suggested that the smaller particles have a smaller surface potential because they adsorb a greater amount of salt per unit area.

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[5] Taylor: J. Phys. Chem., **30**, 145, (1926).

STREAM POTENTIAL DETERMINATIONS ON GLASS CAPILLARIES OF VARIOUS SIZES

BY H. L. WHITE, FRANK URBAN AND E. T. KRICK

An earlier report[1] stated that no stream potential could be detected (method sensitive to 0.1 mv.) across a cellophane membrane through which 0.0005 M KCl was being forced at a pressure of 8 cm. of Hg. When this solution is forced through a glass capillary at this pressure a stream potential of about 125 mv. is developed. The hypothesis was suggested that the failure of the potential to develop across the membrane was due to the discharge through relatively inactive pores of the E.M.F. set up across the active pores. This conception would explain the absence of potential regardless of the reason or reasons for the variations in the behavior of the pores. One factor affecting the magnitude of the stream potentials developed by the various pores might conceivably be pore size. Since it was impossible to investigate experimentally the individual pores in a membrane, glass capillaries were employed as pore models. Previous workers have found stream potential independent of capillary diameter, so long as Poiseuille's law held. Their "small" capillaries, however, did not differ greatly in size from their "large"; no previous workers have used capillaries near our range of small sizes. Our previously reported attempts to investigate stream potential as a function of capillary diameter were unsuccessful because we had not succeeded in establishing the conditions essential to reproducibility of results. During the past year we have succeeded, but only after many fruitless endeavors which need not be described. Most previous workers in this field have had, one would judge from their reports, but little difficulty in getting reproducible results. Our experience has more resembled that reported by Lachs and coworkers.[2]

For our work i.e., the comparison of the stream potentials exhibited by glass capillaries of various diameters, all other factors constant, it was necessary that a method of treating the capillaries be developed which could be depended upon to give repeatedly the same potential for all capillaries of a given diameter. This imposes much more stringent conditions of reproducibility than are demanded in work involving the comparison of various solutions passed consecutively through one and the same capillary. After trying many procedures, including various treatments with chromic acid solutions, we have adopted the following standardized technique. Water at 60-80° is first sucked through the capillary for an hour. The capillary with its glass holder is then sealed to an all-glass apparatus, as shown in Fig. 1, and steam is forced through it at a pressure of 35 cm. of Hg. The water used is double distilled, the second distillation being in a pyrex still from alkaline $KMnO_4$

[1] Bishop, Urban and White: J. Phys. Chem., **35**, 137 (1931).

[2] Lachs and Kronman: Bull. intern. l'acad. polonaise, (B) 289 (1925); Lachs and Biczyk: (B) 360 (1930); Physik. Z., **28**, 556 (1927); Z. physik. Chem., (A) **148**, 441 (1930).

solution. The period of steaming is 60 minutes; the coil of resistance wire around the capillary is heated just red for three periods of 10 minutes each alternating with periods when the wire is not heated. The capillary with its holder is then removed and set aside in the air until the next day when the experiment is carried out. This treatment is repeated before each stream potential determination. We have found a somewhat higher potential when the determination is made immediately after the steaming process but the range of fluctuation of repeated determinations is somewhat greater than if the capillary is allowed to sit for a day. The sucking through of saturated or half saturated chromic acid solution at 90° for one hour followed by prolonged rinsing and sucking through of distilled water gives satisfactory reproducible results for capillaries of ordinary size; the stream potential of many capillaries with such treatment is about 10 per cent lower than with the steaming treatment.[1] With the smallest capillaries, however, (4.5 — 15μ) the chromic acid treatment gave much lower values than steaming and the variation was greater. Whether or not this is due to inability to remove the last traces of chromic acid from their walls we cannot say. All solutions were made up with double distilled water and the water and solutions never allowed to touch anything but pyrex glass.
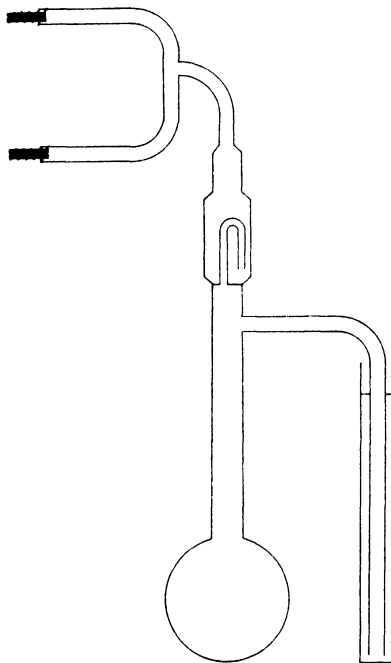
FIG. 1
Apparatus for steaming capillaries

Lachs and Biczyk[2] state that the CO_2 content of freshly distilled water profoundly influences the stream potential of dilute salt solutions, and aerate the solutions with untreated room air before using them. We have found that the stream potential of the relatively concentrated solution (0.0005 M KCl) used in all our experiments here reported is unchanged by prolonged aeration. We

[1] This higher potential after steaming is not always exhibited. Certain capillaries have repeatedly shown the same value with the chromic acid treatment as with the steaming. In the large group of capillaries which we have used are certain exceptionally well behaved individuals which will always show essentially the same stream potential, even with slight modifications in the preliminary treatment. Even these capillaries, however, show the following differences after steaming and after chromic acid; after steaming the initial readings are higher and fall to the stable or equilibrium level in the course of 15 to 60 minutes, while after chromic acid the potential rises to the stable level. Most capillaries are extremely susceptible to slight changes in treatment. We have made so many determinations on many of our capillaries that we know the dependable and the undependable ones; it has sometimes happened that the same piece of glass tubing has furnished capillaries of both types.

[2] Loc. cit.

have also found that removal of possible traces of ammonia and sulphur compounds, as well as of CO_2, from the compressed air by a train of wash bottles containing, in order, 1 per cent iodine plus 10 per cent KI, $N/5$ $Na_2S_2O_3$, 50 per cent KOH, 5 per cent H_2SO_4 and distilled water did not affect the stream potential. It eventually became evident that the fluctuations shown by a given capillary must be due to changes in its walls; these were finally minimized by the treatment described above. In all experiments the pressure applied was 60 cm. of Hg.

The arrangement for measuring potentials was essentially that described in an earlier communication, i.e., the balancing of the stream potential and potential led off from a L. & N. type K potentiometer across a 2 mf. condenser, which was discharged through a 10^{-10} amp. sensitive galvanometer. The leads from the capillary were through $N/10$ KCl calomel electrodes; possibility of diffusion of KCl from the electrodes into the capillary has been certainly excluded. All units of apparatus were mounted separately on one fourth
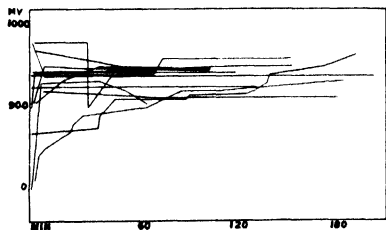
Fig 2

Time-potential curves obtained on different days with an 83μ capillary, No. 5

inch glass plates supported on sulphur blocks. In the latter part of this work, when we came to a comparison of the smallest capillaries with larger, a large and a small were mounted on the same holder and the determinations on the two were carried out simultaneously. The technical difficulties of the preliminary treatment and of the potential measurements increase enormously as the capillary diameter falls below 15μ; with this arrangement we had a control determination with a dependable capillary for each determination on a very small capillary. In this way adventitious departures from standard conditions could be recognized. With every determination on the small capillaries, nos. 24, 26, 28, 36, 38, 40, 42 and 46 a simultaneous determination with a 110μ capillary which gave essentially reproducible potentials was carried out.

Fig. 2 shows the curves of stream potential against time given by an 83μ capillary, no. 5. Table I gives the data on all the capillaries. Each figure represents the stable or equilibrium value of potential exhibited through most of the course of a 2 to 5 hour run. It is not necessarily either the highest figure obtained or the reading at the end of the experiment, although in many cases the highest and lowest figures in a 5 hour run did not differ by more than 4 or 5 per cent. An inspection of Fig. 2 will make obvious the meaning of the term "stable value."

While it is true that reproducible values are obtained with the larger capillaries and even with those of 10μ diameter, this cannot be said of those with diameters of 6μ or less. It is seen that capillaries nos. 36, 38, 44[1] and 46

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[1] This capillary had a circular cross section of 5μ at each end and of 3μ in the middle.

TABLE I
Stream Potentials of Glass Capillaries of Various Sizes at 60 cm. Hg. Pressure

Capillary No. 3

Diameter   47.4μ
Length 5.9 cms.

Date	Reading mv.
10-24	938
10-25	900
10-27	986
10-28	985

Capillary No. 4

Diameter   83.5μ
Length 2.84 cms.

Date	Reading mv.
1-26	1001
1-29	980
1-29	930
1-30	930
2-2	900
2-4	930
2-4	890
2-5	914
2-5	900
2-6	898

Capillary No. 5

Diameter 83μ
Length 4.6 cms.

Date	Reading mv.
1-12	964
1-15	961
1-16	933
1-17	924
1-17	905
1-23	943
1-24	948
2-3	940
2-4	947

2-5	945
2-6	937
2-10	910
2-20	944
2-21	906

Capillary No. 7

Diameter $\begin{cases} 67.5\mu \\ 77.0\mu \end{cases}$
Length 3.8 cms.

Date	Reading mv.
1-16	892
1-22	903
1-23	906
1-26	935
1-27	960
1-28	920
1-28	902
1-29	914
1-30	911
2-2	903
2-3	945
2-4	975
2-5	915
2-6	910
2-9	974
2-11	950

Capillary No. 12

Diameter $\begin{cases} 85\mu \\ 84\mu \end{cases}$
Length 5.88 cms.

Date	Reading mv.
2-13	1000
2-14	1026
2-16	1060
2-19	1002
2-21	1015

Capillary No. 14

Diameter 38μ
Length 4.61 cms.

Date	Reading mv.
2-18	1010
2-19	983

Capillary No. 15

Diameter $\begin{cases} 39\mu \\ 38.5\mu \end{cases}$
Length 4.31 cms.

Date	Reading mv.
2-14	928
2-18	920
2-20	955
2-23	890
2-25	948
2-26	930

Capillary No. 16

Diameter $\begin{cases} 112 \times 125\mu \\ 110 \times 123\mu \end{cases}$
Length 5.03 cms.

Date	Reading mv.
2-6	1012
2-9	1062
2-10	1051
2-11	1000
2-12	1025
2-13	1030

Capillary No. 17

Diameter $\begin{cases} 105 \times 120\mu \\ 105 \times 120\mu \end{cases}$
Length 8.87 cms.

Date	Reading mv.
2-16	1071·
2-18	965

TABLE I (Continued)

Stream Potentials of Glass Capillaries of Various
Sizes at 60 cm. Hg. pressure

2-19	995
2-21	1020
2-23	1000
2-26	990

Capillary No. 18

Diameter $\begin{cases} 84.2 \times 84\mu \\ 84 \ \ \times 84\mu \end{cases}$

Length 4.23 cms.

Date	Reading mv.
2-24	1035
2-26	970
2-28	970

Capillary No. 19

Diameter $\begin{cases} 118 \times 110\mu \\ 118 \times 110\mu \end{cases}$

Length 6.3 cms.

Date	Reading mv.
2-24	1048
2-25	1000
2-26	947
3-5	922
3-6	987
3-7	1010
3-9	957
3-11	970
3-12	975
3-14	950
3-27	895
4-3	920
4-7	920
4-9	940
4-10	940
4-11	960
4-13	955
4-22	915
4-23	895

Capillary No. 20

Diameter $\begin{cases} 37.8\mu \\ 38.4\mu \end{cases}$

Length 4.4 cms.

Date	Reading mv.
2-25	975
2-27	980
3-2	920
3-5	967
3-12	917

Capillary No. 21

Diameter $\begin{cases} 105 \times 112\mu \\ 108 \times 115\mu \end{cases}$

Length 5.0 cms.

Date	Reading mv.
3-4	1022
3-6	945
3-9	950
3-13	1029
3-14	1049
3-30	900
4-1	932
4-7	911
4-8	900
4-14	910
4-17	1020
5-6	900
5-7	899
5-9	900
5-25	920

Capillary No. 22

Diameter $\begin{cases} 25 \times 27\mu \\ 30 \times 32\mu \end{cases}$

Length 2.03 cms.

Date	Reading mv.
3-4	948
3-6	890
3-9	900

3-11	915
3-13	930
3-14	905

Capillary No. 23

Diameter 110 × 118μ

Length 7.0 cms.

Date	Reading mv.
3-5	922
3-6	938
3-7	970
3-10	920
3-11	920
3-12	1020
3-13	1065
3-16	920
3-17	927
3-18	910
3-25	950
3-26	990
3-30	926
4-2	898
4-7	970

Capillary No. 24

Diameter $\begin{cases} 15 \times 16\mu \\ 14.6 \times 15\mu \end{cases}$

Length 1.49 cms.

Date	Reading mv.
3-6	920

Capillary No. 25

Diameter 108 × 115μ

Length 6.15 cms.

Date	Reading mv.
4-16	920
4-24	920
5-5	940
5-6	910
5-9	919

TABLE I (Continued)

Stream Potentials of Glass Capillaries of Various

Sizes at 60 cm. Hg. Pressure

Capillary No. 26	
Diameter 10μ	
Length .7 cms.	
Date	Reading mv.
3-10	860

Capillary No. 28	
Diameter $\begin{cases} 10.5\mu \\ 10\mu \end{cases}$	
Length .8 cms.	
Date	Reading mv.
3-17	900
3-18	900
3-19	930
3-25	930
3-26	933

Capillary No. 30	
Diameter $26 \times 26.5\mu$	
Length 1.5 cms.	
Date	Reading mv.
4-1	950
4-7	960
4-8	960

Capillary No. 36	
Diameter 8.8μ	
Length 1.12 cms.	
Date	Reading mv.
3-30	700

Capillary No. 38	
Diameter $\begin{cases} 6\mu \\ 5.6\mu \end{cases}$	
Length 1.1 cms.	
Date	Reading mv.
4-2	750

Capillary No. 40	
Diameter $\begin{cases} 9.6 \times 9.6\mu \\ 10.0\mu \end{cases}$	
Length 0.8 cms.	
Date	Reading mv.
4-3	900

Capillary No. 42	
Diameter $\begin{cases} 9.5 \times 10.7\mu \\ 9.5 \times 10.5\mu \end{cases}$	
Length .74 cms.	
Date	Reading mv.
4-9	900
4-10	910
4-11	900
4-20	915
4-21	908

Capillary No. 44	
Diameter $\begin{cases} 5\mu \\ 3\mu \text{ in middle} \end{cases}$	
Length .7 cms.	
Date	Reading mv.
4-9	790

Capillary No. 46	
Diameter $\begin{cases} 4\mu \\ 4.5\mu \end{cases}$	
Date	Reading mv.
4-14	730
4-28	850
5-4	760

with diameters of 8, 5.8, 5 and 4.5 μ respectively, show somewhat lower stream potentials than do the larger capillaries. Several possible sources of error enter into the determinations on the small capillaries, all of which tend to make the readings too low. First, due to the very high resistances, amounting to many thousand megohms, the danger of short circuiting is greatly increased. We have taken every precaution to prevent this and are certain that the leakages are not more than a few per cent of the potentials measured. Second, the difficulties of an adequate and constant preliminary treatment are much greater with the smallest capillaries. One cannot have the same degree of confidence that a thorough steaming process has been carried out that one has with larger capillaries. Third, there is greater danger of a low potential due to partial mechanical obstruction. Obstructions cannot be detected by determinations of the rate of flow through these capillaries; one must depend upon the behavior of the galvanometer deflections for information as to the potency

of the capillary. The appearance of an obstruction could of course be detected by measurements of the capillary resistance but we are not yet ready to report on resistance determinations in the smallest capillaries. Since we have obtained with these extremely small capillaries potentials only 10 to 15 per cent lower and with the 10μ capillaries potentials quite as high as with the large, we feel that as technical perfection is more nearly approached it will be possible to get the same potentials from the smallest capillaries as from the large. This is only an opinion; further work may show that under no circumstances will the potentials of the smallest capillaries be quite as high.
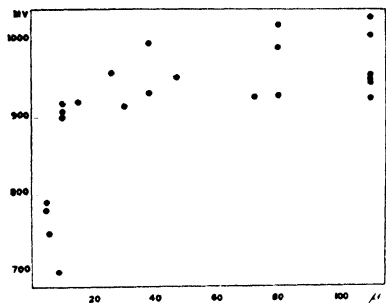
FIG. 3
Each point represents the average of all the determinations on a single capillary, the "stable value" for each determination, as defined in Fig. 2, being used for the averages

Fig. 3 shows the averages of all the data, with stream potential plotted against capillary diameter. Each point represents the average of all the determinations on a single capillary. Whether or not the somewhat lower figures of the smallest capillaries are the result merely of errors due to greater technical difficulties requires further investigation.

The question of the conductance of the fluid column in the capillary is of the greatest importance because surface conductance might be supposed to be a large fraction of the total. McBain, Peaker and King[1] found that the specific conductivity of 0.001 M KCl in a 12.5μ slit of optically polished glass might be 50 per cent higher than in bulk. A quantitative discussion of this question will be deferred until a later publication but it may be pointed out that the ratio of surface to volume in a 10μ capillary is 2 1/2 times that in a 12.5μ slit. If we further consider that McBain and Peaker[2] interpret their more recent work as indicating that the actual surface of ordinary pyrex tubing is about 2.25 times greater than that obtained by microscopic measurement we find that the ratio of surface to volume in our 10μ capillaries was about 5 times as great as in McBain, Peaker and King's 12.5μ slits. Furthermore, since the extent of increase of specific conductivity in narrow spaces increases as the solution becomes more dilute we might reasonably expect the specific conductivity of the 0.0005 M KCl in our 10μ capillaries to be at least between 5 and 10 times its value in bulk. If this is true and if the classical equation for stream potential still holds in capillaries of this size one should expect the stream potential of the 10μ capillaries to be only 1/5 to 1/10 as great as in ordinary sized capillaries, where surface conductance is an insignificant factor. We find, however, that the potential is the same. The predicted potential for the 4 and 5μ capillaries, on the above considerations,

[1] J. Am. Chem. Soc., 51, 3294 (1925).
[2] J. Phys. Chem., 34, 1033 (1930).

should be lower still, only a few per cent of that observed with large capillaries. The fact that the stream potential is not so lowered means that the previously drawn conclusions as to surface conductance at glass-solution interfaces are incorrect, that there was some fundamental difference in the condition of the glass surfaces in McBain's experiments and in ours, that the classical equation for stream potential does not hold in such small capillaries, or that some other factor or factors, as ζ-potential or dielectric constant, is changed in these capillaries in such a way as to compensate for the increased conductivity and maintain an unchanged stream potential.

The first step in the attempt to answer these questions is the direct measurement of the conductance in these capillaries. This work has been started but is yet in the early stages. We have on several occasions observed that a capillary of 10μ or smaller showed a normal stream potential and that in the course of a few days this fell off sometimes down to zero. On other occasions we have seen the potential of a very small capillary rise in the course of a few days from only a few millivolts to the normal level. The question arises whether these changes are due to changes in surface conductance. It is our purpose to follow the capillary resistance through such cycles. In the only cases where we have determined the resistance of very small capillaries showing little or no stream potential the resistance has been infinite, i.e., many times the calculated. This has confirmed our suspicion that these capillaries were mechanically obstructed.

We have been able to measure the resistance of some of our larger capillaries. One would not expect a surface conductance in an 80μ capillary to be so important as in a 5μ. We have employed two modifications of the same method for the resistance measurements. A known high resistance is put in series with the capillary and the P.D. across the resistance is measured by the same technique employed in the stream potential determinations. To measure the capillary resistance while the pressure is on the stream potential itself is utilized as the source of E.M.F. To measure the resistance of the resting capillary a dry cell of known voltage is put in series with the capillary and known high resistance. Knowing the standard high resistance, the E.M.F. and the P.D. across the known resistance, the resistance of the capillary can be calculated. For capillaries with resistances up to about 1500 megohms a 47 megohm "Electrad" resistance was used as the standard. Its resistance was determined by two methods, on a Wheatstone bridge using one dry cell and a high sensitivity galvanometer, and by the leakage of a charged condenser through the resistance. The condenser was a 0.10 mf. mica; it was charged by applying 300 mv. from the potentiometer circuit. It will be noted that neither method uses a high voltage. The two methods agreed to within 3 per cent; the value of this particular Electrad resistance has been determined many times and found to fluctuate a few per cent around 47 megohms; it is therefore redetermined on each day of capillary resistance determinations. The same method may be applied to the smaller capillaries but requires

standard high resistances of from 1,000 to 15,000 megohms, depending on the size of the capillary. Preparation of these resistances has delayed our work with small capillaries.

We have a few data on resistances of four larger capillaries, 74, 80, 80 and 84μ in diameter. The observed resistance is always less than the calculated. We must state here that possibility of error from these determinations is considerable. Our standard high resistance, 47 megohms, was so low that the P.D. across it was only a small fraction of the total E.M.F. The calomel electrodes did not remain completely isoelectric over a long period; fluctuations of a few millivolts were insignificant in measuring stream potentials of 900 mv. or more but would be very important in measuring an 18 or 20 mv. drop across the standard high resistance. Unfortunately we neglected to determine our electrode potentials often enough during these measurements. These difficulties will not obtain in future work; standard resistances more nearly those of the capillaries are being prepared. These preliminary measurements are introduced here to show that variations in stream potential are not correlated with variations in resistance. For these measurements no attempt was made to obtain reproducible potentials; it was rather our purpose to permit changes in the state of the capillary which would effect changes in stream potentials and to see if these were due to changes in conductance. As is seen in Table II, there is no correlation between stream potential and conductance.

TABLE II
Resistance Measurements

Diameter μ	Length cms.	Stream Potential mv.	Observed Resistance ohms $\times$ 10^8/cm.	Calculated Resistance ohms $\times$ 10^8/cm.
80	3.0	726	2.14	3.12
		670	2.07	
		700	2.02	
		835	2.17	
74	5.9	960	2.54	3.6
		870	2.35	
		900	2.39	
		940	2.69	
		887	2.53	
		984	2.43	
84	5.94	900	2.43	2.81
		781	2.35	
		785	2.34	
		720	2.36	
		650	2.42	
		592	2.58	
		572	2.40	
	2.84	732	2.45	
		746	2.38	
		390	2.38	
80	3.11	700	2.6	3.12

Thus, the 84μ capillary on one occasion had a potential of 900 mv. and a resistance of 2.43×10^8 ohms/cm. and on another occasion a potential of 390 mv. and a resistance of 2.38×10^8 ohms/cm. The drop in stream potential was not due to an increase in conductance; apparently the effective ζ-potential has decreased.

According to the data in Table II we find a significant surface conductance in capillaries as large as 80μ, even when no allowance is made for the "pinch effect." These data, as stated above, may very well be in error so far as absolute values are concerned. If there is a significant surface conductance it should be more significant in 10μ capillaries. If this is true we have the apparent anomaly of a normal stream potential and an increased conductance. If further work reveals that there is a high surface conductance in these small capillaries with normal stream potentials it will mean either that the stream potential equation does not hold or that compensatory changes in some other factor or factors permit a constant stream potential.

The bearing of these results on the membrane hypothesis is still not clear. No great difference in potential with change in size has been brought out but even our smallest capillaries are, of course, far larger than the largest pores in a cellophane membrane. Our experiments have not answered definitely whether pore size is a factor, but experience with untreated glass capillaries leads to the conclusion that inequality of stream potentials across the various pores should be the rule rather than the exception. The conception of short circuits through relatively inactive pores to explain the absence of a stream potential across a cellophane membrane still appears reasonable but has not been experimentally established. We would call attention to two papers by Söllner,[1] which have come to our notice since our first communication was read last June, in which he uses essentially the same conception to explain abnormal osmosis.

Summary

The stream potentials exhibited by pyrex capillaries of diameters ranging from 4.5 to 110μ through which 0.0005 M KCl is forced at 60 cm. of Hg. pressure have been measured. A standardized steaming treatment has been established which permits satisfactorily reproducible results. Stream potential is independent of capillary diameter down to 10μ. Capillaries with diameters between 4.5 and 8μ have shown somewhat lower potentials; whether this is a real phenomenon or due to technical difficulties is not yet clear. On the basis of reports by other workers on surface conductance at glass-solution interfaces one should expect a much lower stream potential with our smallest capillaries. The explanation of the absence of the predicted falling off in stream potential with the smallest capillaries will depend upon the results of resistance measurements now under way.

Departments of Physiology and of Biological Chemistry,
Washington University, School of Medicine,
Saint Louis.

[1] Z. Elektrochemie, **36,** 36, 234 (1930).

MINERAL FLOTATION

BY ARTHUR F. TAGGART

Introduction

Appearing as it did in an art (ore dressing) that utilized mechanical principles almost exclusively in its operation, and developing empirically, flotation was first investigated from the purely physical standpoint. And because the controlling phenomena are almost wholly chemical, progress in understanding was correspondingly slow. Since the chemical aspect of the process has been recognized, however, investigation has made rapid strides, and a sufficient background of knowledge has now been built up so that methods of research and control founded on established chemical principles may be confidently applied.

FIG. 1
Diagrammatic sketch of bubble-column flotation

There are a number of so-called flotation processes, but the essential differences between these methods narrow down on analysis, leaving two fundamental groups, which may be designated as bubble-column processes and pulp-body processes respectively. The former are the simpler both in respect to operation and investigation, and may be taken as the type for study.

Fig. 1 presents diagrammatically a common bubble-column operation of the present day. Finely ground (minus − 0.2-mm.) sulphide ore mixed with three to four times its weight of water (the mixture is called *pulp*), is flowed continuously into one end of a porous-bottomed trough-like tank. Lime (1 to 4 lb. per ton of ore) has usually been added to the pulp during grinding. Xanthate (0.05 to 0.2 lb. per ton) goes in from a few seconds to a few minutes before the pulp reaches the flotation cell. Pine oil (0.05-0.1 lb. per ton) is introduced at the head of the cell with the stream of pulp. Air is blown in at the bottom, as pictured. A watery froth carrying the bulk of the sulphide mineral (*concentrate*) overflows continuously; the residual impoverished solid with water (*tailing*) also discharges continuously. Buoyancy of the concentrate particles is brought about by forming aggregates thereof with the air bubbles. The lime and xanthate are added to induce this aggregation. Pine oil imparts stability to the bubbles.

Levitation

In froth flotation of sulphide ores the material that floats is the specifically heavier part. This fact excludes the hypothesis that the overflowing solid in the bubble-column cell is lifted by the rising fluid current induced by the air bubbles. For if such were the mechanism, it would be the specifically lighter material that overflowed.

The particles that overflow are lifted by the bubbles. The reason for the buoyancy of the bubble-solid aggregates is, of course, simple displacement. But the means of attachment of bubble to particle is more difficult to determine. There will occur to the mind of anyone whose recollection runs back to his days in physical laboratory the floating-needle experiment, and—not too
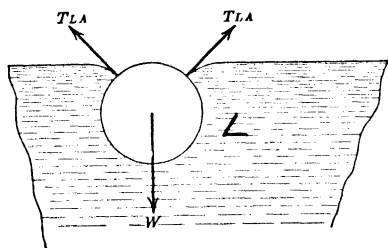
FIG. 2
A floating needle
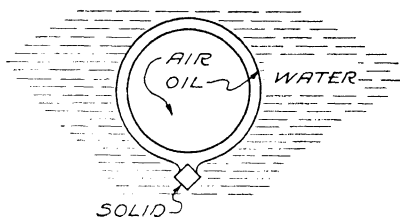
FIG. 3
Probable arrangement of phases in a
bubble column

literally—the same force that held the needle at the surface of the water there holds the concentrate particles in the bubble films. But it is distinctly questionable whether tension of the same interface is effective in both cases. With the needle it was the air-water surface tension, the needle being in equilibrium under the forces pictured in Fig. 2. It is doubtful, however, whether the concentrate particles in a bubble-column froth are in the air-liquid interface; the weight of the evidence is that they are in the interface between a layer of oily liquid forming an inner sheath of the bubble, and the surrounding water. (See Fig. 3.)

Experimental

1. A portion of bubble film may be picked up by dipping a wire ring 1/4 to 3/8-in. diameter into the bubble. If fresh film carrying solid is thus obtained and examined immediately at 30- to 50-× magnification, the air-liquid interface appears unbroken. After 30 seconds to a minute liquid appears to draw away from points of the solid particles that project toward the lens, and these points then protrude into the air. The conclusion would seem to be that the method of examination is capable of distinguishing between an unbroken liquid-gas contact and a solid-gas contact, and that it is the former that exists at the surface, and probably, therefore, in the body of an operating bubble column.

2. A bubble column will not operate if an oil or other substance capable of forming an oily film on the bubbles is missing.

3. The force of the adhesion between solid particles and bubbles in a bubble-column is apparently less than that between the solid particles and the bubbles in a pulp-body operation. (See p. 143.) In this latter type of process the solid particles are in the air-liquid interface. (See Experiment 30, p. 146.) Since the air-liquid surface tension of the

overflow liquid in a properly conducted frothing operation is normally upwards of 60 dynes per cm., while the interfacial tension of the oil used against water is probably not over half that figure, the observed difference in adhesion is significant.

4. If, say, 1 cc. of a non-frothing oil such as Nujol is placed with 5 gm. of a deslimed sulphide ore and 25 cc. of water in a 50-cc. test-tube and the latter closed with a clean cork (not with the thumb) and shaken vigorously three or four times, the oil is broken up into relatively coarse droplets, and microscopic examination (10- to 20-x) shows that sulphide particles are held suspended by these droplets, as is the particle in Fig. 3. If now a minute amount of a spreading oil (see below) is introduced and the tube is again shaken three or four times, the oil droplets differ from those before observed in that, in addition to their solid load, many or all contain air bubbles. These now are obviously in the exact condition pictured in Fig. 3, except that the oil sheaths are relatively thicker. Successive shakings produce progressive thinning of the oil sheaths and more bubbles. Final prolonged shaking will, if conditions are right, produce a mineral-carrying froth of such great bubble surface that the oil layers are so thin as to be invisible under the magnification prescribed. But since the solid particles were seen to be carried, so long as the oil sheath was visible, at the oil-water interface, and since we know, from surface-tension considerations, that the oil film persists, the conclusion seems reasonable that the adhering solid particles remain in the oil-water interface.

Frothing

If pine oil is eliminated from the operation pictured in Fig. 1, all other conditions remaining the same, the volume of the column of bubbles overlying the body of pulp will be materially smaller, so much so that there will be no overflow, and visual evidence of concentration (see p. 143) will be lacking. The pine oil has two functions; it stabilizes the bubble films so that they persist and build up to the overflow level, and it furnishes the oil sheath around the bubbles for holding the solid particles.

The frothing action of a reagent involves spreading of the reagent at the air-water interface, with consequent increase in concentration of the reagent in overflow as compared with the residual liquid. Only those substances which spread are useful frothers. They spread because they lower the surface tension of the air-liquid interface. Their effectiveness as frothers is in proportion to the intensity of their effect on this surface tension, when present in low concentrations. Soluble substances that raise the surface tension of water also have been reported to exert some frothing effect, but are not practical frothers in the flotation art.

Experimental

5. Fig. 4 presents results of surface-tension measurements on overflow and residue liquids from a series of flotation operations in a pneumatic cell, using pine oil as a frother and no other reagents added. Fig. 5 shows the relation between weight of overflow (solid plus water) and difference in surface tension between overflow and residue. The range in quantities of pine oil present, between 20 and 40 mg. per l., is the usual operating range for this reagent, hence it is to be concluded that a reagent that will lower the surface tension between 3 and 5 dynes per cm. at such low concentrations has requisite frothing power.

6. Solutions of sulphuric acid, acid sodium sulphate, and of sodium chloride and sulphuric acid, of 1 to 2 per cent strength, have been used as sole reagents in froth flotation of certain high-grade sulphide ores. The effect of these inorganic substances on the surface tension of the solutions at the concentrations used is an elevation of the order of a dyne per cm. It is distinctly doubtful whether the froths obtained were due to the inorganic

reagents directly. Sensible amounts (from the flotation standpoint) of lubricating oils and greases are present in practically all ores that have been machine mined and milled to flotation size. Such relatively strong inorganic solutions as those under discussion, hot, as they were used, would tend to dislodge such oils from the gangue of constituents of the ores, break up the soaps in the greases, and thus free organic reagents for frothing and collecting, and it is, in all probability, these that were effective.
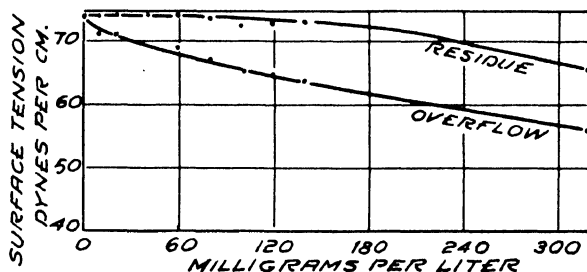
FIG. 4

Surface tensions of overflow and residual liquors from a bubble-column operation
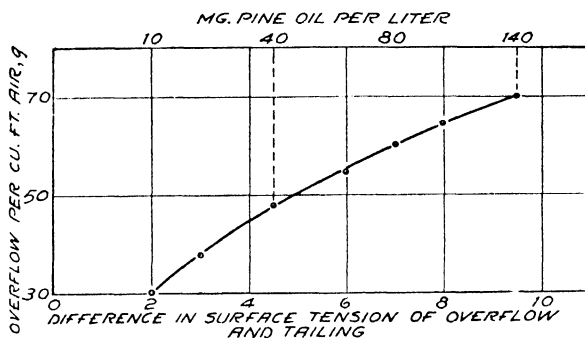
FIG. 5

Frothing on change in surface tension

The way in which the frother functions is best understood by analysis of the ideal experiment pictured in Fig. 6. ABCD is a U-shaped loop of wire set with legs vertical, and EF a straight wire of weight W making frictionless contact therewith. The shaded portion is a liquid film. At equilibrium W = 2 (BC)T, where T is the air-liquid surface tension per unit length of film. If W > 2(BC)T, and the film is a pure liquid, EF will move downward until the film breaks; if W < 2(BC)T, EF will be pulled upward until it makes contact with BC. If, however, the liquid is contaminated with a surface-tension-lowering reagent whose concentration in the surface of the film at a given instant is considered to be represented by the spacing of the shading lines, and if, at the same instant W exceeds 2(BC)T, EF will move downward as before. In so moving it will increase the surface and thereby increase momentarily, at least, the spacing of shading lines, which is to say, the molecules of the contaminant. As a result, since the extent of lowering of the surface tension is

roughly proportional to the concentration of contaminant in the surface, surface tension will increase and tend to counterbalance the excess load. And *vice versa*. Thus a contaminated film has the capacity for automatic adjustment to external strains within its ultimate strength, and in this way its life is lengthened, which is to say that the contaminant adds stability to a froth made with the liquid.

Fig. 7 shows typical surface-tension curves of a good frothing agent (A), a poor frothing agent (B), and an inorganic salt which has some frothing power (C), all with water against air. At low concentrations a change from concentration D to concentration E in the surface of the film produces a large change in surface tension with A, while the changes with B and C are almost negligible.
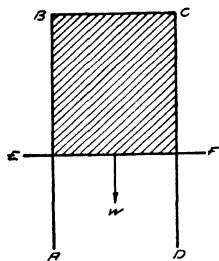
Excluding inorganic compounds, frothing agents have reasonably definite chemical characteristics. The best fall, in general, in the class of organic compounds rated as slightly soluble, and their chemical structure is characterized by a hydrocarbon aggregate of relatively high molecular weight carrying an oxygen-bearing polar group. An investigation[1] of the frothing power of some 500 organic compounds of all classes showed an average of 5.5 carbon atoms in the hydrocarbon aggregate of the molecule of good frothers; the principal polar groups, in order of decreasing frequency of occurrence, were OH, CO, COOH, CONH, COO, and COC; and the solubility centered around 1000 mg. per l.

FIG. 6

The molecule of a frother may be pictured as composed of two different and distinct parts, so far as its reactions toward water and effect on air-water surface tension are concerned. The hydrocarbon part of the molecule resists incorporation with water; the oxygen-bearing part is water-avid and tends to surround itself with water molecules. If the oxygen-bearing part predominates, the entire molecule is drawn into the water and the solubility is high; if the hydrocarbon part predominates too greatly, solubility is very low. With a suitable balance, however, the molecules accommodate themselves readily to the air-water interface, so oriented that the water-avid oxygen-bearing group is in the water and the hydrocarbon in the surface. In such a position the large hydrocarbon groups may be considered as crowding the water molecules apart, thus lessening their mutual attraction, which is to say the surface tension of the liquid, while at the same time no compensating molecular attraction between adjacent molecules of water and hydrocarbon is set up. This is inferable from the low solubility of hydrocarbons in water. The mutual attraction between the organic molecules in the surface (surface tension) is less than that between water molecules. Furthermore these organic molecules are separated by water molecules in the same way as water molecules are crowded apart by organic, so that the presence of the organic molecules in the surface does nothing to compensate for the decrease in surface tension of the water that these molecules cause.

[1] Taggart, Taylor and Ince: Tech. Publ. 204, Am. Inst. Min. Met. Engrs. (1929).

The best frothers so far discovered are alcohols and ketones of the hydro-aromatic series, e.g., terpineol, menthol, eucalyptol, borneol, camphor and the like, and more particularly essential oils containing high percentages of such substances. The straight hydrocarbon constituents in these natural oils are caused to spread at bubble surfaces by reason of the frothing agent dissolved in them, and these oil films seem to furnish better collecting interfaces than films of soluble agents alone. Crude cresylic acid is similarly a more effective frother than highly purified cresols.
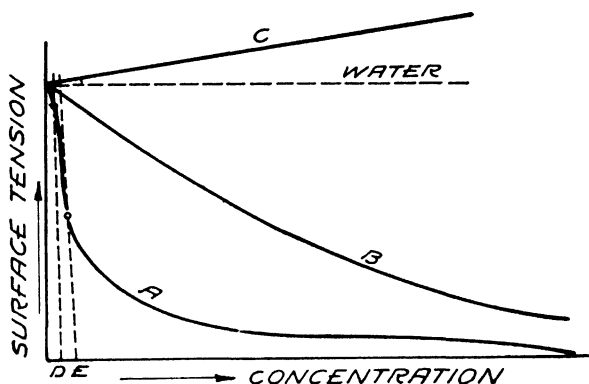
FIG. 7
Surface-tension curves

The frothing effectiveness of the individuals in the lower ends of homologous series increases with increase in molecular weight, which is to say with decrease in solubility. The probability is that frothing-concentration curves for all such series pass through maxima at moderately low solubilities. In all series effective frothing power is substantially zero for the members that are miscible with water in all proportions, and likewise for those members that are actually substantially insoluble. Ordinary handbook ratings of insolubility are not, however, to be accepted as final in this connection, since many reagents used in flotation and dependent for their effectiveness on their solubility are rated in the hand books as insoluble. The proportions in respect to the water in which the reagents are added in modern flotation ranges from I part in 10 000 to 1 part in 100 000 commonly, and only a portion of even these minute quantities seems to be necessary to be in solution at any one time in order to function effectively. Hence no higher member of a promising series is to be rejected without trial on handbook evidence alone.

Experimental

7. Table I shows results selected from a series of carefully comparative frothing tests with the lower members of two allied homologous series. Cresol, with the additional methyl group and resultant lower solubility, is more active than phenol. Xylidin is superior to toluidine, which is superior to aniline. Aniline is less active than its analog, phenol, and toluidine than cresol, indicating the amino group less water-avid, and therefore of less powerful and rapid orienting effect than hydroxyl. Benzene itself has no frothing effect.

TABLE I

Results of Comparative Frothing Tests

Reagent	Conc'n. mg. per l.	Total overflow, gm. per cu. ft. of air	Rated solubilities, mg. per l.
Phenol	200	33.7	60 000
Cresol	25	38 (a)	27 000 (b)
"	200	64.9	"
Aniline	200	27.3	31 000
Toluidine	25	23.0	sl [o]
"	200	38.0	7400 [p]
Xylidin	25	28.6	v. sl.

(a) By interpolation. (b) Mean of [o] and [p].
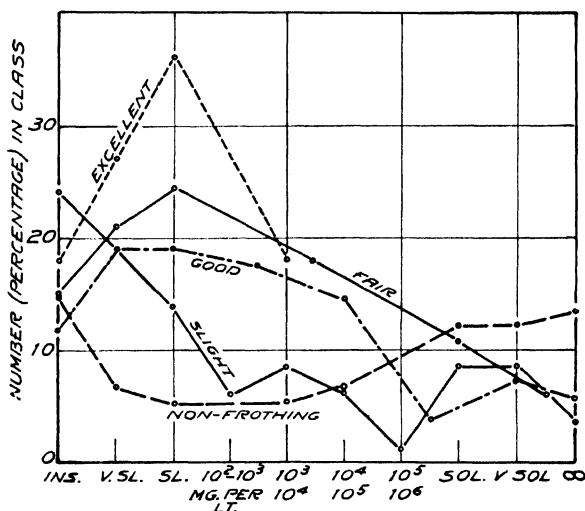
FIG. 8

Owing to difficulties in making quantitative measurements of froth-producing ability, and consequent lack of orderly investigation of various chemical series of frothers, no definite location of the solubility range corresponding to maximum frothing ability can be set forth. Fig. 8 is an approach to quantitative estimation, however, presenting graphically the results of assessments by experienced operators of comparative frothing powers of some 250 chemical compounds of the frothing type.[1] Eleven of these rated excellent, 68 were good, 114 fair, 81 showed slight frothing power, and 74, which had polar-nonpolar structure with oxygenated polar groups, failed. The groups rated excellent, good and fair all show the bulk of the compounds to lie in the solubility range from very slight to slight; here lie also a considerable percentage of the slight frothers. The bulk of the failures lie, as is to be expected, in the insoluble and highly soluble ranges.

The solid-loaded films of a froth-flotation operation are enormously more persistent than any liquid films produced with the same reagents present, but no solid. The reason for the increase in strength is increase in film viscosity

brought about by the solid. The effective phenomenon is probably the same as that in childhood's mudpies. Some heavily-laden froths are so stiff that the froth structure survives dehydration. The closely crowded solid particles key each other into position, while the very thin inter-particle liquid films have characteristically high viscosities.

Experimental

8. If a bubble column made with water and a small amount of frothing agent is stabilized, by regulating the air supply, at a given height in a pneumatic flotation apparatus, addition of a small quantity of finely pulverized solid will cause the height of the column to increase markedly.

9. Float a steel needle on a beaker of clean water (beaker diameter 2 to 3 times the needle length) and place a chip of paraffin wax near the beaker wall. The needle may be rotated about a vertical axis by means of a magnet without moving the chip. Next dust the surface with fine dry solid. Galena that has been washed in a dilute benzol solution of oleic acid and air-dried is good for this purpose. With the surface thus coated with solid the paraffin chip will move when the needle is rotated.

Collection

Potassium ethyl xanthate in the operation pictured in Fig. 1 is known as a collector. If it is omitted and no substitute added, the amount of sulphide mineral overflowed is markedly decreased, and the assay value of the concentrate likewise diminishes greatly. Numerous substitutes for potassium ethyl xanthate are known, ranging from homologous xanthates through chemically similar organic compounds to straight hydrocarbon oils. The oils come first chronologically, but we are largely ignorant concerning the reasons for their action; the xanthates and their like are the modern collectors, and considerable is known concerning the mechanism of their behavior.

Oils

Experiment shows that insoluble highly refined hydrocarbon oils wet sulphide minerals preferentially in the presence of water, while the reverse is the case with gangue minerals. Excluding the possibility of chemical reaction between oil and sulphide—and such exclusion is almost forced, if the oil is of the class described—the action seems to be explicable only on grounds of the interfacial tensions involved. On this basis, applying the law of least energy, it would appear that the energy of an oil-sulphide interface is less than that of a water-sulphide interface, while as respects quartz the relative magnitudes of the interfacial tensions are reversed. We cannot, of course, confirm this reasoning by direct measurement of tensions, and the suggested explanation remains, therefore, a matter of inference.

Experimental

10. If a sulphide-bearing ore is ground in the presence of water with a highly-refined paraffin-hydrocarbon oil (white paraffin, Albolene, Nujol, liquid white vaseline, or the like), and the sulphide mineral is subsequently separated from the gangue and both are analyzed for oil, it is found that the percentage of oil in the sulphide fraction is much greater than in the gangue fraction.

11. If drops of Nujol are brought into contact with plane-surfaced particles of quartz and of galena immersed in water, the droplets spread out into adherent sub-hemispherical segments on galena while on quartz they assume substantially spherical shape and are practically non-adherent. A variety of oils may be substituted for the refined hydrocarbon oil without changing the experimental observations, e.g., creosotes from various tars, essential oils, and liquid fatty oils and fatty acids of relatively high molecular weight. But many, if not all, such substances contain ingredients that might conceivably react chemically with the surface constituents of the sulphide particles; consequently, with respect to such oils, the possibility of chemical action may not be excluded. They probably act, to some extent at least, like the chemical collectors.

Chemical Collectors

The class of reagents of which the xanthates are typical is known in flotation terminology as chemical collectors. Study of a large number of these substances, empirically discovered, discloses that the best fall into a group characterized by the presence in the molecule of a multivalent amphoteric element, combined in negative low-valent or reduced state. Examples are potassium ethyl xanthate in which the S in the SK group is the characteristic element; thiocarbanilid, in which the S, probably in the tautomeric $HS-$ form is the essential atom; and diazo-amino-benzene, containing the active group $-N=N-NH-$.

Experimental

12. In a list of 122 chemical compounds that showed distinct collecting properties on test,[1] there were 193 polar groups. Of these, 98 contained trivalent nitrogen with no other multivalent negative element in reduced state, 26 contained sulphur as the only reduced element, and 13 contained both trivalent nitrogen and divalent sulphur. There were 58 oxygenated groups. The list of polar groups in order of frequency was: NH_2, 29; N, 22; OH, 19; NH, 18; S, 16; $N=N$, 14; NO_2, 13; CSNH, 12; COC, 8; COOH, 7; COO, 6; SH, 5; CON, 4; $N=N-NH$, 4; SM, 4; CO, 3; $-N=NH$, 2; SR, NO_3, $C\equiv N$, I, NO, NCS, CSeNH, each 1. Somewhat more generally arranged, there were 71 amino groups, 17 amides and thioamides, 16 azo and diazo, 16 sulphide, and 11 sulphydrate. The order of frequency is not significant as regards present-day practice. The nitrogen compounds weigh unduly on account of the fact that a large part of the experimentation analyzed was done with a legal slant in which attention was focussed on these substances. Sulphur compounds of the sulphydrate type predominate in practice.

Beside these so-called active groups the chemical-collector molecules must contain a reasonably bulky hydrocarbon portion. The statistical study already cited showed an average of 7 to 8 carbon atoms in this part of the molecule.

The chemical collectors function by forming a substantially insoluble oriented water-repellent film on the surfaces of the minerals to be floated, while at the same time the other minerals remain unaffected. The sulphydrate collectors, which are the only ones that have been investigated with any pretence to thoroughness, form this film by reaction with the surface of the mineral particles that they coat. The reaction appears to be one of ordinary double decomposition, and proceeds to substantial completion because the filming compound formed is more insoluble than either the compound forming the mineral surface in the mill pulp or the reagent itself.

Experimental

13. If a solution of a chemical collector of known strength is shaken with sulphide mineral finely ground in air or in water exposed to the atmosphere, and the solution is then filtered off and tested as to concentration of collector, it is found that collector has been abstracted. This test has been made with α-naphthylamine, potassium ethyl xanthate, diphenyl thiourea, monophenyl thiourea, and thiocresol [p]. Abstraction occurs with galena, chalcopyrite and pyrite but not with quartz or calcite.

14. With potassium ethyl xanthate as the collector and galena as the sulphide, xanthate ion is abstracted from solution and sulphate, sulphite (S_nO_m) and carbonate ions, in total amount stoichiometrically equivalent thereto, are thrown into solution. Potassium remains in solution throughout and lead does not appear in solution. If the galena is ground dry or wet in an atmosphere of nitrogen and the abstraction test is made in the same atmosphere, abstraction is reduced to substantial nullity.[2]

15. If particles of galena are tested as to their reactions toward air bubbles in the presence of water, before and after soaking in collector solutions, it is found that in the presence of such solutions air displaces water from the particle surfaces and the bubbles adhere, while in the absence of collectors the bubbles do not adhere.

16. While the preceding experiment shows that the collector makes the mineral-particle surface water-repellent, and experiment 14 shows that the surface change is due to metathesis, orientation of the surface coating must be concluded by inference. X-ray crystallography indicates that when oxidation occurs at the surface of sulphide minerals, the original sulphide lattice structure tends to be preserved and that the first change is merely substitution of the oxidized anion for sulphide ion with some corresponding expansion of the lattice at the surface. The metal ions retain their original relative positions. When, therefore, the oxidized anions are replaced by collector anions, it is inferential that the resulting compound is oriented at the sulphide-particle surface with the anion toward the solution.

More evidence lies in the fact that if for diphenyl thiourea, which reacts with oxidized lead compounds at galena surfaces to form the corresponding lead-urea salt, which salt adheres to the galena-particle surface and, inferentially, is oriented with the two phenyl groups toward the water, dihydroxy diphenyl thiourea is substituted, abstraction occurs, but the coated particle is not water-repellent. In other words, the substitution of water-avid polar groups on the water end of the phenyl groups causes the result that inference would predict. The evidence for orientation would, therefore, seem to be as complete as is possible, lacking necessarily the ultimate proof of vision.

17. The following abstraction and collection tests were run with galena dry-ground in air; Diphenyl thiourea, 80% abstraction; water-repellency, 100 on an arbitrary scale. Monophenyl thiourea, 83% abstraction, water-repellency 59. Monophenyl urea, 7% abstraction, water-repellency 0. Thiourea, 42% abstraction, water-repellency 0. Urea, abstraction and water-repellency both zero. The thioureas, capable of tautomeric change to the acidic $-SH$ form, all reacted with the oxidized lead coatings on the sulphide particles to form adherent lead salts. The bulky hydrocarbon groups in the phenylated compounds contributed water-repellency. The urea compounds, not acidic toward the lead salts, did not react and were not abstracted and consequently the particle surfaces were unchanged.

It is worthy of note that seleno benzamid (Exp. 12) is an equivalent for thiobenzamid. Phosphorus is to be expected to function similarly, but no useful $-PH$ compounds have been discovered. It was thought at one time that the so-called phosphocresylic type of reagents, formed by treating alcohols with phosphorus pentasulphide might be of this type. But Christman[3] gives to the active substance in these mixtures the general formula $(RO)_2P(S)SH$,

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[2] Taggart, Taylor and Knoll: Tech. Pap. 312, Am. Inst. Min. Met. Engrs. (1930).

[3] Tech. Paper 17, American Cyanamid Company.

with the phosphorus pentavalent, while analyses made at Columbia University of the product formed by treating crude cresylic acid with P_2S_5 indicate that the active collector is a mixture of the three thiocresols. Compounds of the general type RTeH, RAsH and RSbH should almost certainly be collectors, although none have been recorded.

It would seem to follow from the fact that collection involves bringing about a precipitation reaction between the collector and the mineral to be collected, and since the precipitate is a compound of an anion from the collector and a base from the mineral, that in order to test the suitability of a given reagent for a given mineral it would be significant, if not sufficient, to mix dilute solutions (25 to 50 parts per million) of the collector and a soluble salt of the base-metal of the mineral in a test-tube, and observe whether precipitation occurs. A considerable number of such tests have been made at Columbia. The most that can be said as yet is that with some collectors and some bases the test-tube indications are sufficient, but that very slightly soluble and very unstable collectors may give solutions that are so cloudy initially that precipitation with the base-metal salt is not distinguishable, and that certain other collectors require the pH to be within such narrow limits for precipitation—the limits unknown beforehand—that a negative result is not necessarily reliable. On the other hand, the discovery of diphenyl thiocarbazid for differential flotation of siegenite (cobalt-nickel sulphide) from chalcopyrite was determined in the Columbia laboratory by the test-tube method before a single test was run in the flotation cell.

Conditioning

If lime is left out of the operation pictured in Fig. 1—assuming the ore to have been one requiring lime—the amount of metal in the overflow (*recovery*) would have been less and the probability is that the assay of concentrate would have been lower also. Lime in such an operation is known as a conditioning agent. Such reagents perform one or more of a number of known functions, and may also play other parts as yet unknown.

The known functions of conditioning agents are:

1. To react with the mineral to be floated in such a way that the resultant salt forming the modified surface will react with the collector to form an adherent water-repellent film. Such reagents are sometimes called *activators*.

2. To react with one of the minerals in the ore in such a way that while before treatment it would have reacted with the collector and floated, after treatment it will not. Such reagents are sometimes called *depressors*.

3. To react with and remove, by precipitation or otherwise, salts in solution which, if present, would react with other flotation agents. Reagents that act thus may be called *conserving* or *protective agents*.

4. To control the behavior of the finest ("slime") gangue particles toward the minerals to be floated. Since such reagents cause readily visible changes in the degree of dispersion of the slimes they are called *dispersion agents*.

5. To bring and maintain the pH of the solution within such limits that the chemical reactions involved will proceed with maximum velocity and to the requisite extent.

Experimental

18. The best known activator is copper sulphate, which is used to enhance flotation of sphalerite. When used with a collector such as potassium ethyl xanthate, the sequence of known facts is as follows. Powdered sphalerite abstracts copper ion from solution and the concentration of zinc ion in the solution increases correspondingly. According to Zies, Allen and Merwin[4] the reactions are:

$$ZnS + CuSO_4 \rightarrow CuS + Cu_2S + H_2SO_4$$
$$CuS + 7\ CuSO_4 + 4\ H_2O \rightarrow 4\ Cu_2S + 4\ H_2SO_4$$
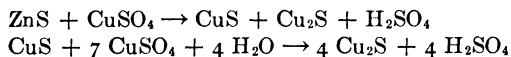
Both reactions are accelerated toward the right by the presence of lime. The concentration of $CuSO_4$ solution in flotation is normally about 1 part in 8000 to 10 000. With concentrated solutions and high temperatures the sphalerite is visibly altered.

The cuprous-sulphide coating on the sphalerite surfaces oxidizes rapidly and the oxidized surface reacts with xanthate to form an adherent film of insoluble, water-repellent cuprous xanthate. These conclusions are evidenced by abstraction of xanthate ion and corresponding appearance of sulphate ion in solution.

Gaudin and Anderson[5] report the use of lead salts to activate malachite, and attribute their utility to exchange of the base-metal ions. Gaudin, Glover, Hansen and Orr[6] report activation of calcite by copper and lead nitrates when soaps are used as collectors.

The early use of sulphuric acid as an activator with insoluble oily collectors probably involved solution, by chemical reaction, of oxidation products from the mineral surfaces, leaving clean sulphide surfaces available for preferential wetting by oil.

19. Depressors react with the minerals that they affect to form adherent salts less soluble than the salts that the collector would form with the base of the mineral. Alkali cyanides are typical depressors for sphalerite. Powdered sphalerite abstracts cyanide ion with corresponding discharge of sulphide and sulphite ions into solution. Zinc cyanide is less soluble than zinc xanthate, hence xanthate ion is not abstracted when the treated sphalerite is immersed in xanthate solution.

Copper sulphate reactivates the depressed sphalerite. Copper sulphate decomposes zinc cyanide, forming first the soluble cuprocyanide ion; further copper sulphate then reacts with the sphalerite as in Exp. 18.

Chromates similarly depress galena, but no reactivating reagent is known.

Organic depressors of the type of urea and the hydroxyphenyl thioureas could be used for metals with which they form adherent salts. The only case of such usage that has come to the writer's attention, however, is that of lactic acid to depress mica in a sulphide flotation operation. It is inferential, without further evidence, that the hydroxy-acid structure of the lactic acid furnishes a reactive polar group that bonds the reaction product to the mica surface, leaving the other water-avid polar group to repel air bubbles.

Certain colloidal materials like glue, albumen, tannin, saponin and the like act as depressors. Their action and control are not, however, understood.

20. Iron salts in solution apparently react with α-naphthylamine and with benzidine, probably also with xanthate, to form compounds of distinctly less effectiveness as collectors than the original reagents. Lime is added to such pulps as a protective agent. It removes the iron by precipitation as hydroxide. Soluble copper and lead consume xanthates, thiocresol and the like by forming insoluble precipitates. Soluble sulphides clear up such solutions effectively. When sulphides are used, however, the pulp should subsequently be thoroughly aerated before a sulphydrate collector is added, otherwise the surfaces of the

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[4] Econ. Geol., 11, 408 (1916).
[5] Tech. Paper 9, (1930), University of Utah.
[6] Tech. Paper 1, (1928), University of Utah.

sulphide-mineral particles are not sufficiently oxidized to react with the collectors. Thus cerussite or malachite soaked in H_2S water and remaining therein show no water repellence when xanthate or thiocresol is added, but if aerated after sulphidizing and then treated with the same reagents, their water repellent quality is high.

21. If a galena particle is immersed in a pulp made of slimed quartz and distilled water (probably a trace of iron is also essentially present), and the mixture is stirred for several minutes, the galena surface after removal of the particle and washing with distilled water will be substantially unchanged so far as microscopic examination can determine. The quartz particles are dispersed and in Brownian movement. If now lime in an amount equivalent to from 1 part in 8000 to 1 in 2000, reckoned on the water, is added to the pulp and the above treatment of galena repeated, the galena surface becomes heavily coated with quartz particles that do not wash off, and the quartz particles in the pulp are flocculated. With certain other slimes of different mineralogical nature, notably ones that contain considerable portions of kaolin, the behavior toward galena and as regards flocculation is exactly reversed.

Slime-coated sulphide surfaces adhere to gas bubbles with difficulty, if at all. Consequently reagents that control slime behavior thereby control flotation.

The mechanism of slime coating is not thoroughly understood. Ince[7] published results of migration tests on quartzitic and clayey slimes as well as on galena and sphalerite suspensions which indicated that when coating occurred the slime and sulphide particles were oppositely charged, and that when both were like charged there was little, if any, coating. The obvious conclusion is to consider coating as simple coalescence or flocculation of unlike charged particles. But the flocculation of the slimes themselves concurrent with coating is not consistent with such a conclusion. Furthermore, subsequent work on the charges on the particles has failed to confirm Ince's findings, and indeed has thrown doubt generally on migration results as applied to this class of materials.

Experimental

22. pH control. Gaudin, Haynes and Haas[8] have published results of a comprehensive investigation of the effects of pH on the flotation of sphalerite, both with collectors alone and with collectors plus an activator. Recoveries with the collectors investigated in the absence of an activator passed through maxima in every case, the pH of maximum recovery being set down after the name of the collector in the following list of those tested: thiocresol [p],6.2; iso-amyl mercaptan, 6.4; potassium-n-amyl xanthate, 4-5; di-iso-amyl ammonium di-iso-amyl di-thio carbamate, 7-9; mono-(9.5-10.5) and tri-iso-amyl amine, 7.8; phenyl hydrazine, 6.2; di-phenyl hydrazine hydrochloride 2.5-3.5; and iso-amyl phenyl hydrazine, 5. On both sides of the maxima the recoveries fell off rather rapidly to negligible figures.

The effect of copper sulphate was in all cases to widen the zone of highest recoveries. With the sulphydrate compounds it additionally raised recoveries in the maximum zone, but with the nitrogen compounds there was no distinct betterment in the maxima.

Thomas[9] recommends close control of alkalinity to the range from 7.5 to 8 for flotation of metallic gold and silver, when lime is used to precipitate iron and copper salts (protective reagent). He states that higher concentrations of lime cause marked decreases in recovery.

While no data may be cited to prove directly that the zones of maximum recovery above recorded correspond to pH bands of maximum reaction velocity

[7] Tech. Pap. 195, Am. Inst. Min. Met. Engrs. (1929).

[8] Tech. Pap. 7 (1930), University of Utah.

[9] U. S. Pat. 1,802,989 (1931).

between the respective collectors and the mineral-particle surfaces, yet such a conclusion and explanation of the facts seem almost unescapably inferential.

Aeration

The operation pictured in Fig. 1 will not be materially affected if nitrogen or oxygen or hydrogen or illuminating gas is substituted for air. Further, froth flotation may be effected with the reagents or their equivalents added in this same operation, if other methods of introducing gas are employed, e.g., if the pulp is boiled, or subjected to a vacuum, or if a gas such as CO_2 is generated in the pulp by chemical reaction of an acid and a carbonate, or if the pulp is beaten by a rapidly revolving stirrer. But the mechanism of mineral-bearing froth formation thus effected is different from that in the operation pictured.

Experimental

23. If sample tubes are inserted at short vertical intervals along the side of a transverse section of the bubble-column machine shown in Fig. 1, and if simultaneous samples are drawn and assayed and the results plotted, they yield a graph like that in Fig. 9. The interpretation of these data is that all of the concentration that is effected takes place in the bubble column.

Visual examination of an operating machine fitted with glass sides shows that the color of the muddy liquid comprising the bubble walls is the same at the bottom of the bubble column as that of the underlying pulp, while, in the case of an ore containing a dark-colored sulphide and a light-colored gangue, the bubble column becomes greatly darker as the top is approached.

24. Fig. 10 is a diagrammatic cross-section of one unit of a typical agitation-froth machine. B is a deep box, square in horizontal section, connected by a hooded slot with the settling box C. Pulp with reagents enters B and after suitable agitation discharges into C where froth rises to the top and overflows, and impoverished pulp discharges at the bottom, to enter an adjoining unit or be sent to waste.

FIG. 9

If, with the ingredients indicated in Fig. 1, an operation in the apparatus of Fig. 10 is sampled along section AA, as in Exp. 23, and the samples are similarly assayed and plotted, the resultant graph is as shown in Fig. 11. This curve is made up substantially of two vertical segments ab and cd with a discontinuity from b to c. Interpreted it means that full concentration is complete at the bottom of the froth layer, the bubbles emerge from the pulp body with their selection already done, in other words, concentration has been effected at the bubble surfaces in the body of pulp itself. Since the same operation can be carried on in the agitation chamber alone by closing the outlet slot and stopping agitation after a suitable time, at which time a mass of froth rises immediately to the pulp surface, it may be further concluded that concentration is effected and completed at the bubble surfaces in the agitation chamber of Fig. 10.

25. The mechanism of particle behavior during concentration in a bubble-column operation may be observed directly by examining the pulp in the bubble walls of an operating column in a glass-sided cell using a magnifying glass of sufficient strength (about 10-×) to resolve individual sand particles. (There is a knack to the observation. The eye must
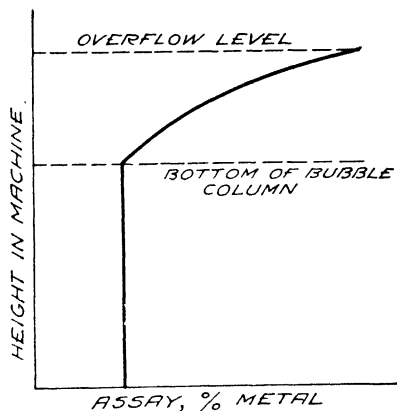
first be accustomed. This is most easily done by choosing a relatively quiescent part of
the column and looking at it with the sole purpose of resolving the coarser individuals.
After this end is attained it is easy to distinguish different minerals and to follow their
paths.) All solid particles are falling; at a rate that seems enormous due to magnification.
But this difference is apparent: That the particles of non-floatable mineral tend to follow
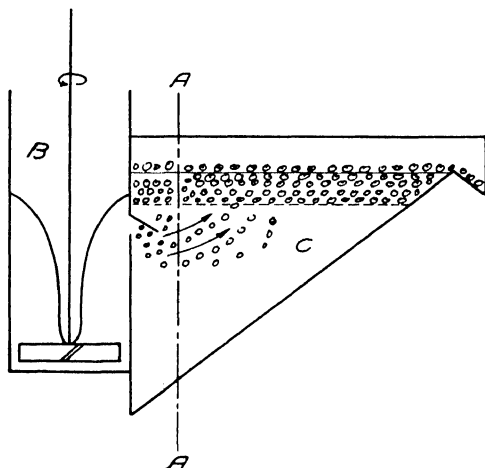
FIG. 10
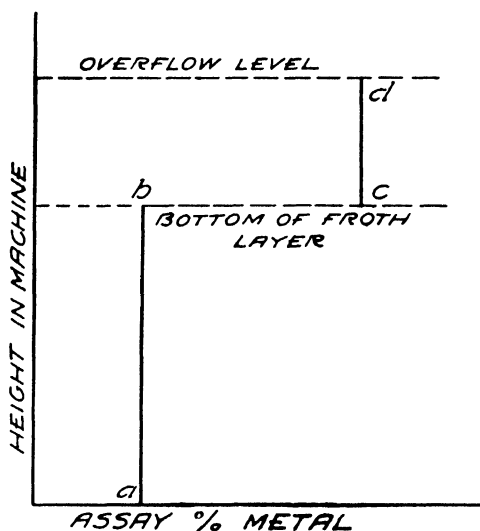
FIG. 11

the middle of the stream and—significantly—having run over the upper surface of a bubble,
they drop directly to the upper surface of the next lower bubble in their path, while the
particles of floatable mineral do not drop off at the horizontal equator of the bubbles but
follow around on the under side and cling sufficiently so that several may collect tempo-
rarily in a little patch at the bottom pole.   This fact alone shows that the floatable particles
are somewhat retarded in their fall relatively to the non-floatable particles, by some attractive
force exerted on them by the bubbles.   The nature of this force is indicated by Exp. 4 to be
the surface tension of the interface between water and an oil sheath surrounding the bubble.

Its effect is to slow down the falling rate of the floatable particles relatively to the non-floatable. By regulating the bubble supply so that the mean rising rate of bubbles in the column is intermediate between the mean falling rates of floatable and non-floatable particles, the former have a resultant rise and the latter a resultant fall, and this effects separation.

The method of bringing about attachment of floatable particles to bubbles in the agitation process and the manner of that attachment both differ from the bubble-column process. So far as it is possible to determine, lacking ability to see into the mechanism as can be done in the latter operation, attachment in the agitation process is brought about by precipitating gas from solution preferentially at the surfaces of properly prepared particles of floatable mineral, and the mineral particles on the bubbles are at the air-liquid rather than at a liquid-liquid interface. The agitation method thus becomes one of the group of pulp-body processes, which includes the boiling, chemical-generation, and vacuum processes, already mentioned. These latter can be peered into with a glass and thus supply grounds for inference as to the mechanism of the first.

26. *Boiling process.* If a sandy pulp—48-mesh, deslimed with suitable collecting and frothing agents is boiled, the floatable mineral collects on the surface of the boiling pulp as a froth. If water containing individual particles of floatable mineral coated with a collecting agent is slowly heated under microscopic observation, bubbles may be seen to form on the particles and grow, some to a size that will lift the particles. Since no bubbles are present at the beginning nor any introduced externally during the operation, those that appear must have come by precipitation from solution in the water.

Sheet platinum may be substituted for the individual floatable particles for microscopic investigation. It has the advantage that it may be cleaned by acid and basic solutions without the danger of reaction, and may be burned for further and final cleaning.

Bubbles do not precipitate on cleaned platinum. Nor on uncontaminated gangue particles. Nor on platinum so heavily coated with oil that the oil consitutes a visible liquid layer.

The froth in the boiling process looks like clotted aggregates or floccules of mineral particles bound by small bubbles. It clearly forms near the bottom of the pulp and rises to the top without change.

27. *Vacuum process.* If a similar sandy pulp similarly prepared is subjected to a vacuum, the behavior is entirely similar to that described in Exp. 26, as is also the behavior of larger individuals observed microscopically. The conclusion is, therefore, again that the concentration is completed in the body of pulp by precipitation of gas on the floatable-mineral particles.

28. *Chemical-generation process.* If a similar ore containing calcium or iron carbonate, similarly suitably prepared, is treated with dilute acid solution, the behavior is precisely similar to that described in Exps. 26 and 27, as is also the behavior of individuals. This is also, therefore, the same kind of a process.

The agitation process makes a froth of the same nature as is made in the other pulp-body processes; concentration takes place in the pulp body; it is primarily inferential that the mechanism of air attachment is likewise the same, i.e., a matter of precipitation. Direct evidence on this score follows:

29. Pressure measurements made by means of an opening drilled in the back of one of the impeller blades in an agitation machine showed that, at operating speeds, there was a gage vacuum of 10 to 12 in. of mercury. The actual vacuum was higher, of course, but was relieved by water vapor and air that distilled into the gas space between the pulp at the impeller blade and the gage.

In an agitation machine sealed to prevent vortex formation over the impeller, a cloud of gas bubbles appeared around the impeller at flotation speeds. With introduction of external air prevented, this air can only have come from solution.

30. A flotation test was made in which external air was introduced in very fine bubbles into a pulp stirred at different speeds. No flotation occurred with the stirring below a speed that recorded pressure drop on the gage. Flotation started at the speed at which pressure drop started, whether external air was introduced or not, and increased in rapidity and extent with increase in speed of rotation.

The agitation process is, therefore, a continuous vacuum process that may be operated at atmospheric pressures. As fast as the air content of the pulp is diminished by precipitation it is replenished by solution of finely divided air taken in by the vortical action of the rapidly revolving stirrer, beaten into fine bubbles by the moving blades, and subjected to super-atmospheric pressure in the zones in front of the blades.

The minerals at the bubble surfaces are probably in the gas-water interface rather than in the oil-water interface, as has been inferred to be the fact in the bubble-column process. The particles are more strongly held, as is to be expected from the higher surface tension of the air-liquid interface. Precipitation must start as a single molecular individual, and assuming a monomolecular oriented film of contaminant on the particle, this individual must be in contact with this film, without any intervention of an oily bubble sheath. The final bubble consists of a number of these individuals added to the first, hence the mass of gas constituting the bubble filling must be in contact with the contaminated particle surface, which is to say that the particle is in the gas-water interface.

The observations on gas precipitation would seem to be rationalized by the following hypothesis, viz.: That such precipitation is effected by reason of a local rise in vapor tension at a solid-liquid interface in a system in unstable equilibrium with respect to vapor tension.

If we consider the system consisting of water saturated with air at atmospheric pressure and the temperature prevailing, and a sheet of platinum with one-half contaminated and one-half clean surface immersed therein, all in a vacuum cell, then as vacuum is applied, vapor-pressure equilibrium between the liquid and its surroundings is upset in such a direction that water must vaporize and dissolved gases must pass out of the liquid, in order to restore equilibrium. Vaporization and gas evolution, under such circumstances, will take place first from those liquid surfaces where vapor tension is highest, which is to say—all other things being equal, where surface tension is least. Disregarding for the moment the walls of the container, there are three surface tensions to consider, viz.: the liquid-gas or upper surface, the liquid-clean platinum interface, and the liquid-contaminated platinum interface.

As to the surface tension of the liquid-clean metal interface, reasoning by analogy only is possible, but such reasoning points toward the conclusion that this tension is higher than the liquid-gas interfacial tension. For we know that in the case of immiscible liquids of different surface tensions toward air, the liquid-liquid tensions lie between the respective two liquid-air tensions. For

example, the surface tension[10] of mercury against air is 513 dynes per cm., of water against air 75 dynes, and of carbon bisulphide against air is 30 dynes. The interfacial tension of water against mercury is 392 dynes per cm.; of carbon bisulphide against mercury, 387 dynes; of water against carbon bisulphide, 42 dynes per cm. The surface tension of platinum against air at the solidifying point[10] is 1690 dynes per cm. Assuming that the surface tension of solid platinum against air is not less than this figure and that the interfacial tension water-platinum lies between 75 and 1690 dynes per cm., in analogy to water-mercury, the vapor pressure at this interface of elevated surface tension will be lower than that of the free gas surface and consequently vaporization should take place at the free gas surface and not at the clean metal surface.

On the other hand, and by the same method of reasoning, the surface tension of the contaminated platinum contact with water is to be expected to be lower than that of the free water surface. For the surface tension of an oil-water contact is lower than that of an uncontaminated water-gas contact. The vapor pressure, rising with fall in surface tension, should be higher at the contaminated metal surface than at the gas surface, and water is to be expected to vaporize there.

Unless the surface is plane, vaporization will start at and be concentrated at the point inequalities (local points of least surface tension and highest vapor pressure due to geometrical configuration). Dissolved air will vaporize rapidly into these incipient bubbles on account of the initial zero partial pressures of air therein, so that the rapid growth of bubbles from mere pin-point size to sensible dimensions, which is the observed behavior, is the expectable result.

The fact that when a solid is coated with a thick layer of oil, so heavy as to be observable as a liquid body, gas precipitation does not take place, detracts in no way from the hypothesis offered. At such a liquid-liquid interface there is no reason for gas molecules to collect as a bubble. Those that leave the water, as individuals, because of high vapor tension, pass, as individuals, into the liquid oil, or *vice-versa*, and partition takes place until equilibrium is established.

The oil-platinum interface is, according to hypothesis, a region of high surface tension and correspondingly low vapor tension, so precipitation of gas that passes from the water into the oil is not to be expected at the oil-platinum interface.

Flotation Machines

Flotation machines are to be classified on the basis of the method used for introducing the gas for buoying the floatable mineral. Two principal types of machines and a class that is a hydrid of the two prevail today. Fifty, however, would not number the species—usually named for their inventors—included in these three genera.

Bubble-column machines. The most widely used and most efficient of the bubble-column genus are the pneumatic machines, of which the apparatus of

"Smithsonian Physical Tables," 146 (1916).

Fig. 1 is typical (Callow). Repetition of treatment is obtained by making the porous-bottomed trough long, with or without subdivision. With coarse feed pulps that settle on the blanket a V-shaped trough is used with a canvas covered air-supply pipe rotating in the bottom (MacIntosh). Rotation sloughs off the settled sand. When pulps containing soluble iron are made alkaline with lime, a mixture of iron carbonate and calcium carbonate and sulphate precipitates in the blanket pores and increases resistance to air flow, with consequent power increase. For such pulps a form of pneumatic machine is used with air introduced through open pipes. In this case enough air must be used and the trough must be so designed as to encompass rapid turbulent circulation of the pulp in order to break up the large masses of air entering at the pipe terminals into small bubbles, and provision must also be made at some point in the circulatory flow for substantial quiescence of the pulp for a sufficient time to permit the finely divided impregnating air to rise and form a bubble column (Forrester, Welsch, Hunt).

Another form of bubble-column machine (Cascade) effects air introduction by discharging a stream or jet of pulp into a body of pulp. The jet breaks up into small masses and drops, each of which acts on entering the body of pulp as a solid particle and drives a bubble of air ahead of it into the mass. The action is familiarly exemplified by the jet from a faucet entering a wash bowl.

Agitation-froth machines. The best-known machines of this class are of the type of Fig. 10 (Minerals Separation). Repetition of treatment is obtained by building a number of units side-by-side with common walls and flowing the discharge from one settling chamber into the bottom of the adjacent following agitating compartment.

Hybrid machines. The sub-aeration type has a cross-section similar to that of Fig. 10. Additional air is introduced through a hollow agitator shaft and a specially shaped impeller (Ruth, Groch, Fahrenwald), or through a pipe entering the agitating compartment below the pulp-level therein (Stenning, Owen, Hebbard, Kraut).

Some agitation machines cascade the pulp from the agitating chamber into the settling box (Janney); others introduce air through a porous medium located in the bottom of the settling compartment (Janney, Jones-Belmont).

Differential Flotation

Differential flotation is the operation of floating one mineral selectively in a pulp that contains two or more minerals of the class ordinarily considered floatable, e.g., galena is floated while sphalerite and pyrite remain submerged; chalcocite and chalcopyrite may be floated away from pyrite; sphalerite, from pyrite and pyrrhotite.

Experimental

31. If a pulp containing galena, sphalerite and pyrite and the usual gangue minerals, made alkaline (pH 8.5 to 10) with lime or sodium carbonate, is digested at normal temperature for a short period (5 to 30 min.) with alkali cyanide, present in the proportions of 0.5 to 2 or 3 parts per ton of ore (and 1 to 3 tons of water), and then floated with 0.05 to 0.1 lb.

potassium ethyl xanthate and an equal·amount of pine oil, the galena floats preferentially. Further digestion of the residue with copper sulphate (1.5 to 2 lb. per ton of ore) present and re-flotation—with more xanthate and pine oil, if necessary—raises the sphalerite. The iron may finally be floated by intensification of the flotation effect, as by the addition of more xanthate and frothing oil, or by addition of 1 or 2 lb. per ton or ore of a collecting oil such as coal- or wood-tar creosote, with or without acidification of the pulp.

Most of the chemical reactions involved in this operation have already been discussed. Zinc cyanide formed on the sphalerite surface prevents formation of zinc xanthate (Exp. 19). Pyrite probably becomes coated with insoluble ferro- and ferricyanides. Galena is not attacked, and thus reacts with xanthate. Copper sulphate subsequently removes the cyanide coating from the sphalerite and coats it with copper sulphide (Exp. 19), which, with the xanthate, furnishes the sphalerite with a water-repellent coating. The action of the iron at this point is not known. Microscopic examination of pyrite in the tailing from zinc flotation shows the surface considerably altered, but still exhibiting patches of pyritic luster. It may be that it is these portions of the surface that become coated with collecting oil or further xanthate, finally resulting in flotation.

Brownian Movement. Microscopic examination of the pulps and products of Exp. 31 reveals varying degrees of Brownian movement. Controlled experiments with the various solid substances separately immersed in solutions of the various reagents, shows that Brownian movement of the solid in given solutions is a distinctive matter, and that direct correlation exists between movement and floatability.

Experimental

32. Galena, sphalerite, pyrite and quartz, dry powdered through 200-mesh (0.074-mm.) screen, were suspended individually in distilled water, the proportion of solid to liquid being 1 to 4 by weight. After allowing a short time for sedimentation, the supernatant cloudy liquids were examined separately by dark-field illumination. Quartz was in motion, the other minerals at rest. Sodium carbonate was next added to all samples in an amount equivalent to 1.5 to 2 lb. per ton on the solid. All four minerals were in vigorous Brownian movement. Potassium cyanide was added next, in an amount equivalent to 1 lb. per ton of solid; the motion of quartz and galena was unaffected, that of sphalerite and pyrite was intensified. Potassium xanthate added to the preceding solutions in an amount equivalent to 0.1 lb. per ton of solid stopped the motion of the galena but did not affect that of the other minerals. Pine oil in the same proportion, added additionally, caused no further change. Reference to Exp. 31 shows that galena will float at this point. Further addition of copper sulphate did not affect galena, pyrite or quartz, but did stop the motion of sphalerite. Exp. 31 demonstrates that sphalerite will float at this point.

It thus appears that when mineral particles are in Brownian movement, even though suitable collecting and frothing agents are present in proper amounts, they will not float; and that the converse is also true.

If the classical theory, which ascribes Brownian movement to reaction of suitably sized particles to the impulses of bombarding molecules, is accepted, there is neither rhyme nor reason to the phenomena described. It is true that flocculation was more noticeable when particles were quiescent than when they were in motion, but on the other hand, in pulps in motion, there were

moving floccules much larger than many of the individuals and floccules at rest in quiescent pulps. Even more conclusively against the molecular bombardment theory, however, is the following experiment.

33. Quartz of high purity was broken into lumps of about 1/8- to 3/8-in. size, soaked for several days in chrome acid cleaning solution, washed for several weeks in running tap water, further washed ten or a dozen times by decantation with distilled water, then dried and ground in a porcelain mill to pass 200-mesh. The powder was next ignited for an hour at 1000°C. This powder was in vigorous movement in m/1000 sodium carbonate solution and at rest in m/1000 sulphuric acid.

A slide was made of the suspension in carbonate solution, the cover glass sealed on with paraffin wax, leaving portions of the periphery toward opposite ends of the slide unsealed. The quartz was in active movement. A drop of m/500 sulphuric acid was then placed at each of the unsealed places. The progress of the diffusing acid could be followed across the the slide, using a large-field low-power objective (16-mm.), as a wave front of cessation of movement. When the wave fronts from the two ends met near the center all motion on the slide had ceased.

It is to be borne in mind particularly at this point that the slide had been prepared of such dilution that individual particles were many diameters apart and that the largest were at least 10-times the diameter of the smallest. The behavior of individuals was observed at 2500-×. In ceasing to move they first slowed, seemed to settle, struck bottom (the slide), gave one or two spasmodic wriggles, perhaps even went into suspension again for a few moments, but finally came to rest on the bottom, as individual particles, not parts of a floc.

When all the particles had come to rest the experiment was continued by adding m/500 sodium carbonate solution as the sulphuric acid solution had previously been added. Now a wave-front of resumed Brownian movement passed across the slide until finally the whole field was again in motion, perhaps more sluggish than in the first instance, but nevertheless unmistakable.

The same process of stopping and revivification has been performed in a test-tube, its progress followed by slides prepared at intervals.

It would seem that these experiments throw serious doubt on any hypothesis that ascribes suspension of such particles as these, and their irregular vibratory motion, to direct bombardment by the molecules of the suspending liquid. Particles of a given size were stopped and started again in Exp. 33 with no visible change in their size or state of aggregation, and consequently with no visible change in the conditions which, mechanically, would enable them to resist the effects of impact. Adsorption of a microscopically invisible layer of something in the sulphuric acid solution, with consequent increase of mass, would seem to be disproved by the fact that the range in size of particles in motion both before and after the sulphuric acid treatment was easily ten times the diameter of the smallest moving particle, and adsorption, by whatever mechanism, amounting to a thousandfold increase in mass of any of the particles is inconceivable. Yet increase to a yet greater extent in the mass of the smallest particles is necessary to explain their stoppage on mechanical grounds.

Change in momentum of the bombarding particles would seem to be barred on the principle of equipartition of energy. If, as this principle states,

each of the particles in motion in such a system as we are dealing with has, when the temperature is uniform throughout, the same amount of energy, then changes in association of the molecules of the suspending medium, ion hydration, introduction of new ions and molecules, and the like, will not change the force of the bombardment.

It would seem, further, that attribution of Brownian movement in these pulps to a molecular or ionic bombardment, greater either in its intensity or effectiveness when sodium carbonate is present, than when sulphuric acid is present, is completely upset by the fact that if the chemical nature of the suspended particles is different, if for instance, calcite replaces quartz or galena or sphalerite, sodium carbonate does not produce movement. It is true that the converse cannot be said, viz: that sulphuric acid does produce motion with calcite. But by changing again the nature of the suspended material, this time to a highly silicious volcanic tuff, we have a mineral that moves in the presence of sulphuric acid.

A yet more informative correlation exists between Brownian movement and the chemical nature of the particle surfaces, than has been shown between motion and floatability. When the particle surfaces are coated with a readily ionizable salt whose solubility in the suspending medium lies somewhere between a fraction of a milligram and 20 to 30 mg. per liter, then the particles, if suitably small, move. With surface solubilities outside this restricted range, the same particles are at rest.

34. Galena is at rest in m/1000 solutions of H_2SO_4, K_2SO_4, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $MnSO_4$, $MgSO_4$, $KHSO_4$, $FeSO_4$, Ag_2SO_4 (solubility $PbSO_4$ = 42 mg. per l.); HCl, KCl, $CaCl_2$ (Sol. $PbCl_2$, 6730 mg. per l.); HNO_3 (sol. $Pb(NO_3)_2$, 390 000 mg. per l.); K_2CrO_4 (sol. $PbCrO_4$, 0.2 mg. per l.); S:C (OC_2H_5) SK, (sol. [S:C (OC_2H_5) S]$_2$ Pb, 0.2 mg. per l.). Galena is in vigorous motion in m/1000 Na_2CO_3 (sol. $PbCO_3$, 20 mg. per l.), and in more sluggish motion in $K_4Fe(CN)_6$ (sol. Pb[Fe $(CN)_6$]$_2$, "insoluble").

Precipitated lead carbonate, made by reacting lead nitrate with sodium bicarbonate and washing the precipitate 6 times with 50 to 100 volumes of distilled water per wash, then filtering and drying at 100-110°C, then grinding in agate, is at rest in distilled water and in m/1000 alkali sulphate, iodide (sol. PbI_2, 440 mg. per l.) and chloride solution; it is in vigorous movement in m/1000 solutions of Na_2CO_3, $NaHCO_3$ and $(NH_4)_2CO_3$, NaOH (sol. $Pb(OH)_2$, "sl.s"), KIO_3 (sol. $Pb(IO_3)_2$, 12 mg. per l.), K_2CrO_4, K_2HAsO_4 (sol. $PbHAsO_4$, "i"), $Na_2C_2O_4$, (sol. PbC_2O_4, 1.6 mg. per l.), Na_2HPO_4, $K_2Cr_2O_7$ (probably forms the chromate).

Precipitated lead chromate acts similarly to the carbonate.

Precipitated lead iodate moves in m/1000 Na_2CO_3.

Precipitated lead sulphate does not move in distilled water, nor in m/1000 solutions of K_2CrO_4, Na_2CO_3, NaOH, or $NaHCO_3$.

Sphalerite is at rest in the same solutions as those listed in which galena is at rest. The solubilities of the sulphate, chloride, and nitrate of zinc are higher than those of lead; the solubility of zinc xanthate is about 330 mg. per l.

Sphalerite moves in m/1000 Na_2CO_3 (sol. $ZnCO_3$, 10 mg. per l.), NaCN (sol. $Zn(CN)_2$, "i"), NaOH (sol. $Zn(OH)_2$, 4.2 mg. per l.), and $K_4Fe(CN)_6$ (sol. Zn[Fe $(CN)_6$]$_2$, "i").

Quartz is at rest in m/1000 H_2SO_4, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, HCl; HNO_3. It exhibits vigorous motion in distilled water and m/1000 Na_2CO_3 and NaOH. It has appreciable motion in m/1000 $ZnSO_4$, $MnSO_4$, $MgSO_4$; KNO_3 and feeble motion in $CuSO_4$, $KHSO_4$, $CaCl_2$ and KCl.

A kinetic picture that, lacking all direct proof, yet corresponds to the observed facts, is that particles in Brownian movement are, for all practical purposes, visible ions,—inert masses, so far as their visible portion is concerned, but having anchored in the surface of their lattice structure, in greater or less number, one of the ions of a compound that is formed by reaction of the original particle-surface compound with one of the constituents of the suspending medium. The other ion of this reaction product may be pictured as diffusing throughout the suspending medium, subject to the forces that cause diffusion, and, by inter-ionic attraction, transferring the effect of these forces to the visible ion.

If it is contended that diffusion itself is due to molecular activity (bombardment), and that the present picture, therefore, differs only in detail from the classical presentment, the author has no quarrel with such a stand. But from the viewpoint of interpretation of flotation phenomena the difference in detail is vital. For it forces us to regard each and every particle in a flotation pulp as a potential participant in one or more chemical reactions which fundamentally determine the behavior of the particles in the flotation operation. And it gives us a key to control. If we would float any particle we must cause it to react with some added ingredient to form a compound substantially insoluble and non-ionizable in the suspending medium, and having, furthermore, such surface characteristics that the energy of the interface between it and air or a frothing oil is less than that between it and water.

If we would prevent a particle from floating, several courses are open to us. (1) We may use a collector that does not react with the particle or with any reaction product of the particle with any of the other ingredients of its environment. (2) We may use a collector that, although it reacts with one of the ions of the particle, does not form therewith a substantially insoluble compound (e.g., potassium ethyl xanthate with sphalerite). (3) We may add, prior to the introduction of the collector, a substance that reacts with the particle surface to form a compound less soluble than the reaction product of the collector with the unaltered particle.

Further applying the same principles we may float a particle not normally floatable with a given collector by first adding a reagent that will react with the particle surface to deposit there, in the form of a relatively insoluble yet slightly ionizable compound, an ion which forms with the collector a less soluble or less ionizable compound that is water-repellent. (Copper sulphate with sphalerite and xanthate; lead or copper salts with calcite and xanthates.)

Logical extension of the principles here laid down leads to the conclusion that flotation or depression of any mineral involves solely investigation of its reaction possibilities and of the properties of its reaction products. Ordinary lists of chemical compounds and their solubilities will be extremely helpful in such an investigation, but failure to find publication of a given salt is not to be accepted as conclusive evidence that such a salt may not be formed;

characterization in a table as "insoluble" does not necessarily mean insolubility in the extremely low concentrations of the flotation cell; and finally a solubility figure based on ordinary methods of determination is not necessarily the figure that will obtain when precipitation or non-precipitation at a mineral-particle surface is involved. The only certain test of reaction and precipitation is an abstraction test made with the mineral itself, under conditions of reagent and hydrogen-ion concentrations, ultimately, that approach those in the flotation cell.

Direct tests on the water-repellent character of coatings may be made in the apparatus described by Taggart, Taylor and Ince.[1] When suitable mineral particles are not available, actual testing in a flotation machine must be resorted to, but conclusions in this case are necessarily a matter of inference.

OPTICAL SENSITIZATION IN PHOTOGRAPHY*

BY WILDER D. BANCROFT, J. W. ACKERMAN AND CATHARINE A. GALLAGHER

In 1873 Vogel[1] published a short paper on the sensitization of silver bromide plates by certain dyes. "I obtained from England some silver bromide dry plates prepared commercially by Wortley, who used a process some details of which are kept secret. I exposed these to the spectrum and found to my surprise that they were more sensitive in the green to the E line than in the blue to the F line. The sensitivity, contrary to all previous experience, was greater for light which usually is rather inactive chemically than for light which is usually very powerful chemically. This phenomenon caused me to study more carefully the sensitivity of silver bromide to spectrum colors.

"I experimented with silver bromide in two forms: (1) as a so-called wet plate, moist with the silver nitrate solution from the bath in which the plates were sensitized; (2) as a dry plate, prepared by washing off the silver solution and drying. The dry silver bromide showed a much greater color sensitiveness than the silver bromide under the silver solution. With an acid developer the sensitivity of the wet plate ended about half-way between D and E, practically in the middle of the yellow. The dry plate was sensitive two millimeters beyond the D line, into the orange.

"The behavior of the two plates was qualitatively very different. With the moist silver bromide there was a very strong action between G and F (in the indigo and blue); at F it decreased very rapidly and there was only a slight fogging beyond E. With the dry silver bromide the action in the blue was much weaker than with the wet plate; but the decrease was much less in the longer wave-lengths and the effect extended beyond D, as has been said. Dry silver bromide is therefore more sensitive for the less refracted wave-lengths and the wet plate for the more refractive, the blue, rays of the visible spectrum.

"Silver nitrate is a powerful sensitizer for ordinary photographic plates and increases the sensitivity because it combines chemically with the iodine or bromine set free during the exposure. The reason why this effect takes place chiefly in the blue is because the blue rays are absorbed more strongly by the film than the others.

"This explanation for the action of silver nitrate on silver bromide made me suspect that the English silver bromide plates must contain a substance which absorbs green more strongly than blue. Dry plates are often covered with all sorts of substances, such as tannin, gallic acid, caffeine, and morphine,

[1] Ber., **6**, 1302 (1873).

all substances which combine with iodine and bromine and which therefore sensitize. Occasionally people add a yellow dye to cut down the amount of the chemically active blue light. Practically nothing is known about the optical behavior of these 'preservatives,' and there is no certainty that they are beneficial.

"The Wortley plates contain uranium nitrate, rubber, gallic acid, and a yellow dye as a covering. To determine whether this covering had an effect, I washed a Wortley plate with alcohol and water, obtaining thereby a plate with no increased sensitivity in the green. I then attempted to impregnate silver bromide with a substance which would absorb the yellow rays chiefly and would combine with free iodine or bromine, in the hope of increasing the sensitivity in the yellow. I selected corallin which Professor Liebermann most kindly placed at my disposal. A very dilute solution showed an absorption band between D and E; in more concentrated solutions the absorption extended beyond D; on the other it was quite transparent to the blue at F.

"I dissolved corallin in alcohol and added enough of it to my bromide collodion to color the latter a strong red. With this collodion I prepared silver bromide dry plates which were colored distinctly red. On exposure to the spectrum, my prediction was verified. The sensitivity of the plates was marked in the indigo and decreased towards the blue, being quite weak at F. From there on the sensitivity increased, becoming almost as great in the yellow as in the indigo. A method had therefore been found for making silver bromide plates as sensitive for yellow, a hitherto chemically inactive color, as for indigo which had been considered the most active color chemically.

"After these experiments I believed that a dye, which absorbed red strongly and which reacted with bromine, would increase the sensitivity of silver bromide for red. I found such a substance among the green aniline dyes. It absorbed strongly the red rays in the middle between D and C. With higher concentrations the absorption extended further towards D; but yellow, green and blue were transmitted with very little loss. A collodion dyed with this green was actually light-sensitive into the red. The sensitivity decreased from indigo to yellow and then increased, there being a strong effect in the red where the absorption band occurred.

"From these experiments I believe myself justified in concluding that we are able to make silver bromide light-sensitive to any color one pleases, or to increase the existing sensitivity for any particular color. It is only necessary to add a substance which will promote the chemical decomposition of the silver bromide and which absorbs the color in question without absorbing the other colors appreciably. Perhaps we may be able some day to photograph infra-red as we now photograph the ultra-violet.

"It should be possible also to overcome the disturbing effect due to the photographic inertness of certain colors. The following experiment shows what can already be done in this line. I photographed a blue band on a yellow ground. With an ordinary silver iodide collodion plate I obtained a white band on a black ground. With a silver bromide corallin plate, on which blue and yellow are equally effective, I obtained of course no contrast. I then put

before the objective a yellow glass which cut off most of the blue and let the yellow pass practically unchanged. After a sufficiently long exposure I obtained a dark band on a light ground."

We have only to consider the panchromatic films, the orthochromatic films, and the films for aerial photography which are sensitive in the extreme red, to see how accurate Vogel's forecast was.

Carey Lea[1] did not believe in Vogel's conclusions. Describing his work, he said: "It seemed therefore a matter of interest to determine whether any general law existed that when a metallic compound capable of reduction by light was placed in contact with a body capable of being oxidized (or of uniting with chlorine, bromine or iodine) the capacity of the metallic compound by any particular portion of the spectrum would be influenced by the *color* of the body placed in contact with it. If, for instance, a ferric salt be placed in contact with an oxidizable body of well-marked color, will the reducibility of the ferric salt by particular rays be modified? And if so, will it follow the law announced by Dr. Vogel for silver bromide? To solve this question, I have made an extended series of experiments. But I have not been able to verify the existence of such a law.

Ferric Salts

"Ammonia ferric oxalate was selected as the most easily reducible of the ferric salts.

"Strips of paper were first thoroughly colored with aurine, with aniline blue and aniline green; they were then impregnated with the ferric salt, and were exposed to light side by side with ordinary white paper similarly impregnated with the ferric salt.

"The exposure of these and of all the following preparations was managed in the following manner. Colored glass was obtained of shades corresponding as nearly as possible with the colors of the spectrum. Violet and green glass could be found in commerce of suitable shades. The other colors were obtained by dissolving suitable transparent pigments in varnish and coating glass with it. With the aid of aniline colors and colorless varnish, the most brilliant shades were obtained, with a perfect transparency. These glasses were next cut into strips ten inches long and five-eighths wide and arranged to form a sort of artificial spectrum, under which papers of different preparation could be simultaneously exposed. It is evident that in some respects this mode of operating is less advantageous than that of exposure to a real spectrum. But the disadvantage is compensated by the possibility afforded of a most accurate comparison of the effects of the various substances, inasmuch as the different papers can all be exposed simultaneously and all receive precisely the same impression. There results an accuracy of comparison which can perhaps be obtained in no other way.

"The papers prepared with ferric salt alone, and also those with ferric salt in contact with the colors named, were simultaneously exposed. They

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[1] Am. J. Sci., (3) **7**, 200 (1874); **9**, 355 (1875); **11**, 459 (1876).

were then plunged into solution of ferricyanide of potassium, which renders evident whatever reduction has taken place by the production of Turnbull's blue, the unreduced portions remaining white.

Result.—"The series of experiments was carefully repeated three times. The aniline blue was found to be entirely without influence; the printed spectrum obtained corresponded in every respect with that of the plain ferric salt. The aniline green slightly diminished the impressibility, but not more in one part than another. Aurine produced this effect still more strongly.

"Neither coloring matter exerted any specific influence on the impressibility by any particular portion of the spectrum.

"Other coloring matters were tried without results of special interest, except that a cold aqueous extract of *safflower* (carthamus) much heightened the sensitiveness to the whole spectrum, perhaps doubling it.

Silver Chloride

"A number of experiments led to the following results: Coralline increased the sensitiveness to all the rays, but especially to blue and violet, in which the increase is very considerable.

"Rosaniline increased the sensitiveness to blue and violet, but diminished all the rest.

"Aniline blue diminished sensitiveness to green, increased it to yellow, and was without effect on the rest.

"Aurine diminished sensitiveness to all.

"Mauveine and aniline green were without effect.

"Litmus reddened by acetic acid strongly increased the sensitiveness to the blue and violet, and somewhat diminished it to the red and orange.

"Here we have three red colors increasing the sensitiveness to the blue and the violet. But one, coralline, increases the sensitiveness at the red end also, whereas red litmus and rosaniline diminish the sensitiveness at the red end.

Silver Iodide

"Silver iodide papers, imbued with various coloring matters and containing free silver nitrate, were exposed to the different rays with the following results:

"*Red and Orange rays.* None of the coloring matters tried increased the sensitiveness to these rays.

"*Yellow rays.* Aniline blue and green increased the sensitiveness to these rays somewhat, mauveine perhaps a very little. Coralline diminished the sensitiveness a little, aurine and rosaniline a good deal.

"*Green rays.* The aniline green (a bluish green) increased the sensitiveness to the green ray somewhat, aniline blue (a violet blue) increased it a very little. Mauveine was without influence, whilst coralline, aurine and rosaniline gave weaker results than the plain iodide paper, the last two much weaker.

"*Blue rays.* Aniline green is here again the strongest. Blue and mauveine increased the sensitiveness to the blue rays a little, coralline was without effect, aurine and rosaniline diminished the sensitiveness.

"*Violet rays.* Aniline blue, green and mauveine all considerably increased the sensitiveness, coralline increased it a little, aurine and rosaniline diminished it a little. With ordinary white light the order of sensitiveness was the same as in the violet rays.

"It does not appear that there exists any general law connecting the color of the substance placed in contact with the silver iodide with increased or diminished sensitiveness to particular rays. A violet blue aniline color increased the sensitiveness to the yellow and green rays, but also had a similar effect upon the violet rays. Aniline green increased the sensitiveness to the violet, blue, green and yellow rays, but not to the orange and red; its tendency was to increase the sensitiveness of colors approximating to its own color, whereas coralline increased the sensitiveness to the rays which most differed from its own color.

Silver Bromide

"Silver bromide is at once the most important of all the sensitive substances known, and the most difficult as to the exact determination of its reactions, so much do these vary from very slight causes. Multiplied experiments were consequently made; thirty-five complete spectra were obtained, besides prints from detached portions of the spectrum. Below I give the substances in the order of the greatest sensibility which they conferred, beginning with those that gave the greatest.

Substances which conferred the greatest sensibility to the more refrangible half of the spectrum	Substances which conferred the greatest sensibility to the less refrangible half of the spectrum
Infusion of tea leaves,	Salicine,
Salicine,	
Red Litmus,	
Coralline,	Plain bromide,
Aniline blue	
———	———
Plain bromide,	Aniline green,
———	Mauveine,
	Aniline blue,
Aniline green,	Aurine,
Mauveine,	Infusion of tea leaves,
Aurine,	Coralline,
Cold infusion of safflower,	Infusion of capsicum,
Infusion of capsicum	Cold infusion of safflower (carthamus).

"The substances above the 'plain bromide' increased its sensitiveness, those below it diminished it, and in all cases to an extent corresponding with the order or rank in the respective columns.

"Generally speaking, the substances enumerated above exerted very much the same effect on different colors at each end of the spectrum, that is, those that heightened or impaired the sensitiveness to the green acted similarly on

the yellow, orange, and red, and those that heightened or impaired the sensitiveness to the violet rays acted similarly to the blue rays and also to white light.

"The conclusions which I have reached seem to me to establish that there is no general law connecting the color of a substance with the greater or less sensitiveness which it brings to any silver haloid for any particular ray."

While testing a number of red dyes to find a sensitizer for green rays, Carey Lea found that coralline would work but did not consider its action as any function of its color because it exhibited a "still more marked tendency to increase the sensitiveness of silver bromide to the red ray than to the green." He reported that none of the other red dyes used in that experiment had any sensitizing effect.

Obviously, the outcome of Carey Lea's work was a contradiction of Vogel's law and an apparent disproof. He had no explanation to offer in place of that put forth by Vogel, however, and Vogel's law still seems both plausible and possible.

Not much progress has been made since Vogel's time toward solving the mysteries connected with optical sensitizers. The most recent views are involved and complicated to say the least, and must remain largely hypothetical, since they are, as yet, incapable of being tested experimentally. The following quotation is taken from a recent article by S. E. Sheppard[1] of the Eastman Kodak Company research laboratories.

3. Optical Sensitization

"The silver halides are normally photosensitive chiefly in their own absorption region in the blue-violet. Sensitivity to longer waves can, however, be increased by various processes of so-called optical sensitization. The best known of these is the use of certain groups of dyes, which sensitize the silver halide for an extended spectral region which, while not identical with the absorption spectrum of the dye in ordinary solvents, is conditioned by this, and is probably identical with the absorption of dye: silver halide combination.

"In papers by Fajans and Frankenburger[2] on the influence of ionic adsorption on the photochemical decomposition of the silver halides, conceptions were advanced which open up a new view of these optical sensitizing effects.

"They suggested that adsorption of simple cations, as Ag ions, is limited to an electrostatic monatomic layer. The work required, $h\nu$, for transfer of an electron from a bromide ion to an *absorbed* Ag^+ ion is less than in the case of the normal surface of the lattice.

"The considerations advanced by Fajans and Frankenburger do not, however, seem entirely adequate, for the following reasons. First, the actual surfaces developed in silver bromide crystals are not of the chessboard type described, with alternate Ag^+ and X^- ions. This would be a cubic surface, whereas the faces which are found are dominantly octahedral, i.e., all Ag^+ ions or all Br^- ions. Hence the figure and explanation advanced by Fajans and

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[1] Chemical Reviews, 4, No. 4 (1927).

[2] Z. Electrochemie, 28, 499 (1922); Z. physik. Chem., 105, 255, 373, 329 (1923).

Frankenburger are not realized, except perhaps to some extent for adsorption of Ag$^+$ ions. But if we consider less an adsorption that an inbuilding of foreign nuclei in the crystal grating, then the quantum changes, i.e., diminution of h necessary for the reaction Br$^-$ — $\ominus$ → Br, etc., becomes in *virtue of the deformation of contiguous ions of* the crystal lattice. We have here an explanation of the optical sensitizing presented by the very dissimilar substances, *viz.* metallic silver, silver sulfide, silver iodide, and silver cyanide.

"The writer has indicated elsewhere how this effect may not only lead to anomalous optical sensitizing effects, but also contribute to the *concentration* of the blue-violet photochemical decomposition about the sensitivity centers, notably of silver sulfide.

"In normal or dye sensitizing there is probably no such inbuilding, but a surface adsorption of the dye. The principal classes of sensitizing dyes are:

    A.   Phthaleins, e.g., erythrosin, eosin

    B.   Cyanins e.g., carbocyanins, isocyanins

"The first are acid dyes, forming complex anions. These will be adsorbed chiefly by silver ions, and it is known that these dyes do not sensitize well by bathing, but are assisted by the use of soluble silver salts, i.e., by intermediate silver ions. Going to the pronouncedly basic cyanine dyes these form complex cations, and are therefore held by bromide ions. But, such an adsorption involves reciprocal deformations in the bonded ions, so that the displacement of the spectral sensitizing curve is to be expected. *Hence, we probably get a superposition of the anomalous and normal optical sensitizing effects.* The normal effect follows as an inner photo-electric effect in the dye ion, whereby its reduction potential is raised and silver ions are reduced, which form a latent image about 'sensitivity specks' just as in the case of the photochemical decomposition of Ag$^+$ Br$^-$.

"We may suppose that dyes are either:

    a.   Adsorbed to the Ag$^+$ ions

    b.   Adsorbed to the Br$^-$ ions

    c.   Adsorbed to homopolar AgBr (or AgI)

Acid dyes, e.g., erythrosin, giving (complex) anions, would be expected to adsorb to Ag$^+$ ions, and it is a fact that their sensitizing action is supported by free silver ions.

"Basic dyes, e.g., pinachrome, giving complex cations, would be expected to be adsorbed to Br$^-$ ions in the silver halide lattice. It is, however, a noteworthy fact that such dyes are much more soluble (on the alkaline side) in chloroform than in water. *Hence, one may anticipate a possible strong adsorption to homopolar AgX pairs,* a fact in agreement with the strong adsorption of 'basic' dyes to silver iodide. It is also significant that the sensitizing spectra of these dyes with silver bromide approaches more nearly to the absorption spectrum in chloroform than to that in water or alcohol.

"The exact mechanism of optical sensitizing is not yet clear. The relatively simple cases of sensitization by mercury atoms excited to the resonance

potential and producing active hydrogen by radiationless collisions have been adduced as significant for photographic sensitizing with the dyes. We have, however, in the dye:silver halide complex, a very complicated system, in which we can scarcely picture activated dye molecules, as wholes, colliding with the silver salt. We must rather conceive of a number of changes being excited by absorption of light, ranging from a transmission from non-polar linkages (as in photography) to reversible electron transfers (reduction and oxidation) and finally to non-reversible changes (hydrogenation and de-hydrogenation). If this series is borne in mind, representable by three energy levels of disturbance of the dye:silver halide system, then the radiation antagonism in dye sensitizing and desensitizing effects appears as a combination of the true (virtual) photo-chemical equilibria with pseudo-antagonistic reactions (destruction of photo-product by certain radiations, as in photo-catalyzed auto-oxidations) and with secondary topochemical effects (Lüppo-Cramer's nucleus isolation)."

In a later discussion[1] of the mechanism of sensitizing Sheppard says:

"Provisionally, the mechanism of optical sensitizing, on the basis of adsorption is as follows: Supposing that the colored dye cation is electrostatically held to bromide ion, but that this original electrostriction passes into homopolar combination, in agreement with the conclusion that the colored form is notably less polar than the colorless, on absorption of light by this in its own absorption region an electron is freed, possibly from the bromide ion, and a silver ion reduced, or indirectly by the 'reduced' dye cation.

"This mechanism would give only one Ag atom for each dye molecule adsorbed to the silver halide. Recently Leszynski has published evidence that (with erythrosin) up to 20 silver atoms may be photochemically reduced per dye molecule acting as sensitizer. He suggests that the photoelectron may travel some distance through the silver halide crystal, and effect a chain reaction of rather high efficiency, or that the reduced silver continues to act as an optical sensitizer.

"As an alternative to this, it may be suggested that in the photodecomposition of adsorbed dye on silver bromide, the dye molecule is practically *exploded* with release both of several free electrons, and also of very active free radicals. The photochemical efficiency might then be considerably greater than unity, but would be a pronounced function of the *intensity* of the illumination.

"That the optical sensitizing is connected with the photodecomposition of the dye is supported by the fact that the addition of silver ions to aqueous solutions of the dye greatly accelerates its decomposition (bleaching) by light. Our experiments on this indicated that below a molar ratio of about 1.5 Ag^+ to 1 mole dye, little or no acceleration of decomposition was produced, while from this point the acceleration was approximately proportional to the silver concentration. Whether the apparent threshold is significant or not has not yet been determined."

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[1] J. Phys. Chem., **32**, 751 (1928).

Two years later Sheppard wrote:[1]

Optical Sensitizing

"In gaseous systems an atom of a gas such as mercury, absorbing in its series spectrum, or a molecule of chlorine absorbing in its band spectrum, becomes excited. This excited molecule can transfer the absorbed energy in a single act to another molecule, by a type of inelastic collision, whereby the assaulted molecule is decomposed. It is still an open question whether the optical sensitizing of silver halides by colloid metals, colloid silver sulfide, and by dyes is due to excitation and rayless collisions or to another process, perhaps a photoelectric effect. It appears to be a condition of optical sensitizing by colloid silver and the like that the sensitizer be sub-divided to amicroscopic particles, containing very few atoms, and perhaps monoatomic in one dimension. Fajans and his collaborators have found that silver halide with silver ions adsorbed is sensitized for visible decomposition by longer waves, while adsorbed thallous ions sensitized both for visible and latent image formation. He attributes this to a deforming action of the surface cations on adjacent halide ions, the deformation being greater than in the symmetrically arranged interior of the crystal. The deformed halide ions are supposed to lose electrons for a lower energy quantum. It is also possible that it is due to a reduction of the electrostatic energy by lattice loosening. Fajans has applied the deformation concept to the case of colloid silver sensitizing, assuming deformation by adsorbed silver. Since there is no quantitative evidence on the adsorption of silver, the application remains hypothesis.

"It is also possible that the sensitizing is due to a photoelectric electron emission from the silver, below its critical threshold at about 3300 Å., equivalent to 3.6 volts. This appears reasonable for metal particles in a salt of high dielectric capacity. In this case, however, it appears that only a redistribution of silver atoms should take place, since for each electron emitted by a silver atom a silver cation remains. Delicate methods for determination of free silver have been developed by Weigert and Lühr which may give quantitative data on this point.

"The status of dye sensitizing is much the same. A great amount of valuable technical information has been obtained and the number and efficiency of such optical sensitizers enormously increased, but the theory of their action is still obscure. The hypothesis of collisional transfer of energy has been applied here also, but is difficult to test. Leszinski, working in Eggert's laboratory, found that the absorption of light by one dye molecule (of erythrosin) could give at least 20 silver atoms on visible decomposition of silver halide. This requires something more than the collisional transfer of energy quanta—namely, a superposed chain reaction—the mechanism of which is not clear. Sheppard and Crouch have found two conditions of adsorption of basic dyes to silver bromide. One consists in approach to monomolecular layer formation, provided the dye is in true solution—i.e., if its 'concentration' at equilibrium is below its actual solubility. Above this—

[1] Ind. Eng. Chem., 22, 555 (1930).

from colloid solutions of the dye—multimolecular adsorption of the dye molecules occurs. The maximum effect in optical sensitizing is reached far below this level of concentration and much below formation of a complete molecular layer. This indicates that sensitizing is effected by monomolecular patches of relatively few dye molecules. If the collision hypothesis is correct, it would seem that any strongly adsorbed dye could act as a sensitizer for its own absorption band. This is not the case. Although many classes of dyes give more or less feeble sensitizing, many strongly adsorbed dyes do not sensitize. Actually only two groups of dyes are now practically employed as sensitizers, the phthalein and the polymethine or cyanine type dyes.

"The presence in these of co-ordinatively saturated and co-ordinatively unsaturated atoms of nitrogen (also oxygen, in phthaleins) joined by a system of conjugated double bonds, makes rather plausible Baur's[1] theory of photosensitizing as an intramolecular electrolysis. A continuous system of conjugated double bonds is equivalent, in a single molecular structure, to a metallic conductor, since it permits transmittance of an electron along it according to the potential at a given point. The length of this system will determine the mean resonance frequency for light waves. Given two atoms, which are capable of two valency stages, sufficiently separated by such a chain, then electrolytes could be attached by 'Anlagerung,' and activation by light absorption could bring about actual decomposition.

"My colleague, A. P. H. Trivelli, has discussed[2] a similar possibility for micellar photo-elements, with colloid silver and silver sulfide, which would bring optical sensitizing by these in line, formally at least, with Baur's interpretation. Historically, it appears that this is in direct line of descent through Bancroft with Grotthuss' electro-chemical theory of photochemical reactions. This is the sad part of the theory, that it is a return to a quite primitive conception."

Sheppard is quite right in saying that one possibility is a return to what he considers the primitive concepts of Grotthuss. As a matter of fact Grotthuss gave the true explanation of Vogel's discovery implicitly over a half century before the phenomenon was observed. Grotthuss found that ferric chloride in water is practically non-sensitive to light because the reduction of ferric chloride to ferrous chloride would be reversed at once by the free chlorine or by its reaction products with water. Grotthuss did not speak of decomposition voltages or depolarizers because they had not been invented at that time; but he dissolved ferric chloride in alcohol and exposed again to the light.[3] "In alcoholic solution ferric chloride is reduced by light to ferrous chloride. The reason for the difference is that chlorine reacts readily with alcohol but not readily with water. On the other hand Grotthuss found that ferric sulphate in alcohol was only acted on very slowly by light. The reason for this is that alcohol is not a good depolarizer for oxygen but is a good one

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[1] Helv. Chim. Acta, 1, 186 (1918).

[2] Z. wiss. Phot., 26, 381 (1929).

[3] Bancroft: J. Phys. Chem., 12, 230 (1908).

for chlorine. . . . The light-sensitiveness of all substances is increased by the presence of a suitable depolarizer, and, in many cases, we get light-sensitiveness only in presence of depolarizers."

Grotthuss was using a colorless depolarizer in the case of alcohol and therefore the light absorbed by the alcohol had little or no effect. In his experiments the ferric chloride was oxidizing the alcohol. If he had used a colored depolarizer, the light which was absorbed by the depolarizer would have activated it and would have increased its tendency to reduce ferric chloride. If this activation were sufficient, he would have got photochemical reduction of ferric chloride by the light which was absorbed by the colored depolarizer, in other words the Vogel phenomenon.

We have been familiar with this for years in another form. If we do not use ultra-violet light, which might cause formation of ozone, the light effective in the oxidation of dyes[1] by air is light which is absorbed by the dye. The dye reduces the oxygen instead of the oxygen oxidizing the dye. We do not ordinarily speak of this as a case of optical sensitization of oxygen by a dye because we are not interested in the reduction of oxygen by light, whereas we are interested in the reduction of silver bromide by light.

The general theory of the Vogel phenomenon was formulated clearly[2] over twenty years ago.

"The experiments of von Hübl[3] show that the sensitizing action of a dye may be modified very much by the quantity of the dye in the gelatine acting as a screen. A photographic plate is only sensitized by a dye if the silver bromide is itself colored. . . . The Grotthuss theory requires that the sensitizers should be depolarizers. They must be decomposed by light and must either be reducing agents or must be converted into reducing agents by light. It is not necessary that the order of light-sensitiveness should be identical with that of the sensitizing power. This latter depends on the [chemical] potential while the rate of decomposition depends also on the unknown 'chemical resistance.' On the other hand, a general approximation between the light-sensitiveness and the sensitizing power is to be expected and is found. Dyes, which stain silver bromide and which are not depolarizers, directly or indirectly, are not sensitizers."

Putting this into more modern phraseology, an optical sensitizer for a silver bromide film is a colored substance which is adsorbed by silver bromide, which does not bleed appreciably into gelatine, and which is either a powerful enough reducing agent to produce a latent image with silver bromide under the influence of light, or is converted by light into a reducing agent powerful enough to produce a latent image with silver bromide. This of course does not cover cases where there is fluorescence.

This way of looking at things has not been popular with the mathematical photochemist, as is shown by Sheppard's remark already quoted. Neither

[1] Bredig and Pemsel: Archiv wiss. Photographie, 1, 33 (1899); Bancroft: J. Phys. hem., 12, 257 (1908).

[2] Bancroft: J. Phys. Chem., 12, 353, 375 (1908).

[3] Jahrbuch der Photographie, 10, 289 (1896).

H. S. Taylor nor Sheppard look with favor on the concept of depolarizers, perhaps because nobody has yet applied the quantum theory to it. While one could attack this particular problem on the basis of the original Grotthuss formulation that the action of a ray of light is analogous to that of a voltaic cell, there are cases to which this generalization cannot be applied satisfactorily and the modified Grotthuss theory[1] now reads:

1. Only those rays of light which are adsorbed can produce chemical action.

2. Light which is absorbed by a substance tends to eliminate that substance. It is a question of the chemistry of the system whether any reaction takes place or what the reaction products are.

It therefore seemed desirable to do a few experiments in order to show again how simple the phenomenon really is. Contrary to the general view of modern scientific men, we believe that the easiest experiments are the best and that there is no point in doing a difficult experiment unnecessarily.

If we eliminate the gelatine, we avoid the danger of bleeding and the consequent formation of a color screen. If we eliminate the solid silver bromide, we avoid the question of adsorption. If we start with a system which is practically insensitive to light, we avoid differential development and we can expose as long as we like, thus making it possible to study the behavior of dyes which fade very slowly in the light. If we can use a qualitative test for showing reduction, we avoid the time necessary to do quantitative analyses.

This meant harking back to the experiments of Grotthuss. He had shown that there is no reduction by light of ferric chloride in aqueous solution and we have confirmed that, so far as exposures of six hours are concerned. On adding a dye in the absence of air and exposing until the dye was entirely decomposed, it then became a simple matter to test for ferrous chloride with potassium ferricyanide. In every case in which the dye faded, there was a reduction to ferrous salt, just as the theory required.

Since the mathematical photochemist will probably feel that ferric chloride in solution is too different from solid silver bromide in gelatine to justify reasoning from one case to the other, we decided to meet him half way, though without admitting the validity of his hypothetical contention. We therefore used solutions of silver nitrate in water, hoping that perhaps reasoning from a silver salt would seem less far-fetched to the constitutional objector, even though the silver salt was soluble and there was no gelatine.

Mellor[2] says that "silver nitrate blackens if exposed to light, but not if organic matter be rigorously excluded." Cady[3] says that silver nitrate in the pure state is not altered by light.

We obtained the purest silver nitrate possible and exposed it for six hours in the carbon-arc Fade-ometer. At the end of this time the solution was still colorless and unchanged by light. When metallic silver was precipitated in the presence of a dye by the action of light, we knew, therefore, that this was due to the reducing action of the activated dye.

[1] Bancroft: J. Phys. Chem., **32**, 529 (1928).

[2] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," **3**, 463 (1923).

[3] "Inorganic Chemistry," 474 (1912).

All exposures were made in a Fade-ometer rather than in sunlight to insure uniformity and duplication of conditions. A Fade-ometer is a commercial instrument operating on 220 volts A. C., containing a glass-enclosed carbon arc and a means of holding the samples at a fixed distance (10 in.) from the source of light. This machine is made by the Atlas Electric Devices Company. Columbia violet carbons were used, and the globe enclosing the arc was of Corex glass, which transmits more ultraviolet light than any other type. The transmission percentage for the different wave lengths was worked out by the Bureau of Standards at Washington, the measurements being made on May 25, 1926 between eleven and twelve a. m. Their results are given in Table I.

TABLE I

Spectral Range	% of Total Radiation	
	Arc	Sun
170 to 320 mμ	0.0	2.0
320 to 360 mμ	2.0	2.8
360 to 480 mμ	18.5	12.6
480 to 600 mμ	9.3	21.9
600 to 1400 mμ	16.5	38.9
1400 to 4200 mμ	22.1	21.4
4200 to 12000 mμ	31.6	.4

The arc stream developed produces a spectrum containing qualitative rays of natural June sunlight, but the light of the Fade-ometer is more intense than sunlight, twenty hours exposure in the instrument being equal to about 50 hours in June sunlight. The humidity was controlled by keeping three receptacles under the globe constantly filled with water. Because a great deal of heat was generated by the arc, two fans placed on opposite sides of the instrument were kept constantly running and two of the windows were left uncovered in front of them so that the air currents resulting would meet in the center and carry the heat out the top of the Fade-ometer. The temperature conditions were satisfactory under these conditions. (The newer model Fade-ometers come all equipped with suction fans for heat removal.)

We wanted to expose our solutions in the absence of oxygen so that if a reaction did occur we could be sure that it was due to the sensitizing power of the dye and not merely to oxidation. It was therefore necessary to remove all the air from the flask, which we did by displacing it with nitrogen. In order to do this we needed an exposure flask having an inlet tube with a stopcock and an outlet stop-cock. We used 50 cc absorption flasks which had had stop-cocks sealed onto the side arm leading in. These flasks come with ground glass stoppers which can also be used as stop-cocks. It was therefore possible to bubble the nitrogen in through the side arm (which extends to the bottom of the flask) up through the solution, and out through the stopper, thus effecting removal of the air. The flasks used for the exposure of the ferric chloride

solutions were made of German soft glass, but those used for silver nitrate solutions were of pyrex, which has a higher transmission power for ultraviolet light.

The nitrogen gas used was prepared from liquid air (Matheson Co.) and might therefore contain traces of oxygen. For this reason the nitrogen was passed through two absorption bottles each containing 150 cc alkaline pyrogallol. Before discontinuing the treatment with the nitrogen gas, a small flask containing copper gauze in a solution of cuprous tetrammino sulphate was attached to the end of the system. If the evolving gas still contained traces of oxygen this solution would become blue.

Preparation of Pyrogallol and Cuprous Tetrammino Sulphate—

    1.—800 gr. KOH in 1000 cc water solution.
      150 gr. Pyrogallic acid per liter of KOH solution.
    2.—Approximately 10% saturated copper sulphate solution
            35% ammonium hydroxide (15N)
            55% water

Put the mixture in a bottle with some freshly cleaned copper gauze, stopper, and shake until it becomes colorless. If the blue color does not disappear in half to three quarters of an hour, adjust concentration slightly by adding small amounts of ammonium hydroxide or water until it is such that the copper gauze can effect reduction to the colorless solution on further shaking in the stoppered bottle.

Preparation of Solutions—

All the dye solutions used in this research were of the same strength—.1 gr. per liter.

The ferric chloride solutions were 5% (by weight) ferric chloride and 95% distilled water.

The silver nitrate solutions were 5% (by weight) silver nitrate and 95% distilled water.

Procedure and Data for Ferric Chloride Solutions—

Five cc dye solution were added to forty-five cc ferric chloride solution, making a total of fifty cc, 10% of which is the dye solution of strength 0.1 g per liter. The actual concentration of the dye in the flask ready for exposure is therefore 0.01 g per liter, a very weak solution, which is desirable in sensitizing work as mentioned previously.

The air was then removed from the flask as described above, and the preparation placed in the Fade-ometer for exposure. After exposure the solution was tested for the presence of ferrous ions with potassium ferricyanide. The results obtained in these experiments are given in Table II.

In every case the dye caused a sensitizing of the ferric chloride solution which resulted in its reduction to ferrous chloride.

Water solutions of the same dyes were exposed simultaneously with the ferric chloride solutions to see whether the observed effects were partially due to the natural fading of the dyes or solely to the reaction with ferric chloride. It was found that the colors of the dyes in water did not change noticeably in

the time of exposure, and we conclude that the action was entirely due to the sensitization of the FeCl₃ by the dyes. It was found later, however, that all of the dyes were sensitive to light on long enough exposure. This is in accordance with Vogel's theory which holds that all depolarizers must be light-sensitive.

<div align="center">TABLE II</div>

<div align="center">Ferric Chloride</div>

Name of Dye	Time of Exp.	Color Change	Test for Fe·· ion
Eosin	5 hrs.	Sol'n became cloudy.	Positive
Methyl Violet	4 hrs.	Green to orange of FeCl₂ sol'n in 45 minutes.	Positive
Magenta		Changed immediately on addition of dye—5 minutes.	Positive
Methylene Blue	4 hrs.	Yellowish green to greenish amber in 45 minutes.	Positive
Acid Green	40 min.	Dull olive green to orange.	Positive
Cardinal Red	1 hr.	Dark orange brown to orange.	Positive
Brilliant Green	1 hr.	Light olive green to orange.	Positive
Aurine	2 hrs.	Dye too weak to change color of FeCl₃ in first place.	Positive

<div align="center">Sensitizers from Eastman Kodak Company</div>

Erythrosin	30 min.	Reddish orange to yellowish orange.	Positive
Piancyanol	30 min.	Cloudy orange to clear reddish orange.	Positive
Orthochrome T Bromide	45 min.	Cloudy orange to clear reddish orange.	Positive

These experiments on ferric chloride solutions and dyes illustrate that sensitizers are reducing agents in the broad sense of the term, and that the light-sensitiveness and sensitizing power of a dye need not run strictly parallel; also that if the limiting physical conditions connected with a photographic plate be lessened, the number of dyes that can act as sensitizers will be increased. All the results are in accordance with the principles laid down by Grotthuss, and uphold Vogel's ideas.

Before proceeding with the repetition of the above tests on silver nitrate solutions, we performed a few experiments with color screens to bring out the fact that it is the light absorbed by the dye which actually is effective in bringing about the sensitizing and the chemical reaction. To test this, samples of ferric chloride and dye, with and without a color screen of the same dye were exposed. According to theory, if methyl violet is used as a sensitizer, it is the light absorbed by the methyl violet that would cause the sensitizing action. Therefore a small test tube containing ferric chloride and methyl violet (in the same proportions as in previous experiments) was tightly corked and submerged in a flask containing methyl violet in pure water, the concentration of the dye in the outer flask being greater than that used as sensitizer.

The combination was then exposed simultaneously with a flask containing ferric chloride and sensitizer without the color screen. The time required for fading was compared, and as expected, was greater when the color screen was present to absorb part of the rays normally absorbed by the sensitizer. This experiment was repeated on several different dyes, always with the same result. The inner solutions were 10% dye solution and 90% ferric chloride solution, while the color screens were 15% dye solution and 85% water. The tabular results are given in Table III.

In every case it took longer, and in 3 out of 5 cases at least twice as long, for the dye to act when the color screen was used as when exposed directly. This shows conclusively that it is the light absorbed by the sensitizing dye which is effective, for if it be withheld, the action is greatly retarded.

Table III
Ferric Chloride

Name of Dye	Fading Time with Color Screen	Fading Time without Color Screen
Methyl Violet	75 min.	20 min.
Methylene Blue	230 min.	185 min.
Acid Green	20 min.	10 min.
Cardinal Red	30 min.	20 min.
Brilliant Green	30 min.	10 min.

However, if the action were entirely due to the light absorbed by the dye, there should have been no action at all in the presence of the color screen. We concluded, therefore, that the light absorbed by the ferric chloride must also be effective. The experiments were repeated, using two color screens, one of dye as before, and an additional one of ferric chloride solution. The dye solution was placed in a large test tube and a smaller test tube containing ferric chloride immersed in it. A still smaller tube containing the dye-ferric chloride solution was then dropped into the center and we had a system consisting of a dye color screen, a ferric chloride color screen, and a solution of dye in ferric chloride. The relative sizes of the tubes selected were such that there was about a half centimeter between their walls, thus allowing a sufficiently thick color screen.

The concentrations were the same as those in the previous experiments with color screens. The ferric chloride used as a screen was a $7\frac{1}{2}$% solution.

Table IV
Ferric Chloride

Name of Dye	Test for Ferrous Ions	
	Direct Exp.	With Color Screens
Methyl Violet	+ in 20 min.	− in 40 min.
Methylene Blue	+ in 60 min.	− in 120 min.
Acid Green	+ in 10 min.	− in 20 min.
Cardinal Red	+ in 20 min.	− in 40 min.
Brilliant Green	+ in 10 min.	− in 20 min.

The results obtained with double color screens were very satisfactory and are given in Table IV.

Under these conditions there is absolutely no action, even with twice as long an exposure. This shows conclusively that the action is due partially to light absorbed by the dye and partially to light absorbed by the ferric chloride, and that *only light which is absorbed* is effective in producing the photochemical action.

Procedure and Data for Silver Nitrate Solutions—

The next step was to apply our principles to silver nitrate solutions. Since the restrictions concerned with silver bromide plates are not involved, we should expect any light-sensitive dye which was or became a sufficiently powerful reducing agent to sensitize silver nitrate as well as ferric chloride. As it was out of the question to test every light-sensitive dye, we tried to choose a group which would be representative of all the dyes. We have several basic dyes, several acid ones, and at least one from every important group in dye classifications. Eosin and erythrosin gave precipitates with silver nitrate and therefore were not tested. Pinacyanol and orthochrome T bromide are sufficiently strong reducing agents to reduce a silver nitrate solution in the dark.

The only difference between the performance of these experiments and those on ferric chloride is that 5% silver nitrate is substituted for 5% ferric chloride, and 75 cc pyrex flasks were used in place of the 50 cc soft glass ones. The total volume used was therefore increased to 75 cc but the proportions were unaltered. Oxygen was removed as before. The results obtained are given in Table V.

TABLE V

Silver Nitrate

Name of Dye	Time of Exp.	Color Change	Silver Deposited
Magenta	5 hrs.	Red to colorless	Yes
Methyl Violet	$5\frac{1}{2}$ hrs.	Purple to colorless	Yes
Brilliant Green	$5\frac{1}{2}$ hrs.	Green to colorless	Yes
Methylene Blue	45 hrs.	Blue to very pale blue	Yes
Alkali Blue	$5\frac{1}{2}$ hrs.	Blue to colorless	Yes
Acid Green	$5\frac{1}{2}$ hrs.	Green to colorless	Yes
Cardinal Red	$5\frac{1}{2}$ hrs.	Pink to colorless	Yes
Eosin	None	Colored precipitate separated out. Colorless supernatant liquid	
Erythrosin	None	Cerise colored precipitate settled out immediately. Supernatant liquid colorless and clear	
Pinacyanol	None	Purple to colorless in 3 or 4 minutes —before air could be removed	
Orthochrome T Bromide	None	Scarlet to colorless in 3 or 4 minutes —before air could be removed	

To make sure that the black grains deposited were really metallic silver, the colorless solution containing them was stirred up and a large drop of it placed on a ground glass plate and allowed to evaporate. A dark spot resulted which, when slightly burnished, gave a silvery, metallic lustre. This verified the fact that the precipitate was silver and not some oxide or impurity. Eosin and erythrosin give a precipitate with silver nitrate, and therefore cannot be used in these tests.

Every dye exposed with silver nitrate was found to be a sensitizer as we expected and the results on the silver nitrate solutions are just as satisfactory as those obtained with ferric chloride.

Since ammoniacal copper oxide solution can be reduced to a colorless cuprous oxide solution, we thought it should be possible, by varying the alkalinity and nature of the reducing agent, to get a solution which would not decolorize in the dark, but would in the light. By cutting down a little more we might get a solution which would not decolorize in the light, but which would lose its blue color on addition of a light-sensitive color and exposure to light. This was therefore tested out and found to be possible.

A solution containing 20 cc 5% $CuSO_4$, 10 cc 3N NH_4OH, and 70 cc water was prepared. Ten cc portions of this solution were titrated with a $\frac{1}{2}$% solution of phenyl hydrazine. It was found that when 2 cc were added to a ten cc portion of the ammoniacal copper oxide solution it would fade in the light but not in the dark (within twenty minutes).

The amount of phenyl hydrazine was then cut down to 1.8 cc and the blue color did not disappear upon a twenty-minute exposure in the Fade-ometer. The experiment was then repeated, and a flask containing one cc of eosin was also exposed simultaneously. At the end of twenty minutes neither flask was colorless, but the one containing the eosin was much more faded than the one without it.

This work was repeated using methylene blue and methyl violet instead of eosin. The results were the same. The flask containing the dye always faded faster. If left in the light long enough, they would both become colorless, but the one containing the sensitizer would always lose its blue color more rapidly.

Throughout the entire research we have obtained results which fall in line with the fundamental theories and overthrow Carey Lea's disproof of Vogel's law. However, there is no doubt that his work was carefully done and that he actually did obtain the results stated, but there are several considerations which may account for them.

Some of the observed facts that led him to conclude that the sensitizing action of a dye bears no relation to its color were:

1) Coralline, a red dye, increased the sensitivity of silver chloride and silver bromide for red rays.

2) Coralline, a red dye and therefore expected to absorb green and blue rays, gave no increase of sensitivity to either green or blue light when used with silver iodide.

3)   With silver bromide, the substances giving the greatest increase in sensitivity for the more refrangible half of the spectrum were colorless.

4)   Some dyes, among them coralline, decreased sensitivity to some rays for which they were expected to increase it.

The first objection may be accounted for by the fact that coralline is not a pure substance but a mixture of two dyes and of their oxidation products. Consequently the age as well as the method of preparation cause variations in the composition.   Therefore, although a spectrum analysis of our coralline did not show any absorption bands in the red, it is still possible, and probable, that Carey Lea's coralline did absorb in the red.   This would naturally account for its causing an increase in the sensitivity toward red rays.

The fact that the coralline showed no increase in sensitivity of silver chloride toward green and blue light is nothing to be alarmed about, because it has always been recognized[1] that, not even with light-sensitive substances, are all of the absorbed rays necessarily active.   The presence of absorption bands in the green and blue by no means means that a substance will be sensitive to green and blue light, but only that it *may* be.   It is still true that whatever light does activate it is light which is absorbed, and the action is therefore still related to the color, since the light absorbed indirectly determines the color.

It is perfectly possible that the colorless substances which caused increased sensitivity were reducing agents even in the dark.   They did not give specific action for specific colors.

The decrease in sensitivity observed in some cases can also be explained by the fact that not all the rays absorbed are necessarily active in producing a chemical effect.   They may be absorbed, may not act themselves, and may serve as a color screen for rays of the active absorption band.   Let us imagine a dye having absorption bands in the red and in the green which is only sensitive to green light.   The red light absorbed is inactive, and yet it may serve as a color screen for the green light which would be active if it could get in.   Such a dye might easily cause a decrease in the sensitivity of silver chloride for green light.

Carey Lea should have concluded, not that the color of a dye bears no relation to its sensitizing power, but that the color, or more especially, the light absorbed, is the important and determining factor, although we cannot, as yet, predict what fraction of the light absorbed will cause activation.

The general conclusions of this paper are as follows:—

1.   The Grotthuss theory enables us to account for Vogel's results.

2.   An optical sensitizer in photography—in cases in which fluorescence is barred—is a colored substance which is adsorbed by silver bromide, which does not bleed into gelatine sufficiently to form a color screen, and which is either a powerful enough reducing agent to produce a latent image with silver bromide when activated by light or is converted by light into a reducing agent sufficiently powerful to produce a latent image with light.

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[1] Bancroft: J. Phys. Chem., **12**, 209 (1908).

3. In the cases so far studied it is probable that the silver bromide is reduced by the activated dye and not by a reaction product.

4. In order to simplify the problem we have eliminated the gelatine, the solid silver bromide, and the sensitivity to light in the absence of dye. Aqueous solutions of ferric chloride and of silver nitrate meet these requirements.

5. It has been found possible to do optical sensitization of ferric chloride and of silver nitrate with a number of light-sensitive dyes.

6. It is possible to adjust the concentrations of a solution of ammoniacal cupric oxide and phenyl hydrazine, so that the solution is stable in the dark and bleaches in the light. Addition of sodium eosinate produces optical sensitization.

7. It has been known for years that dyes would act as optical sensitizers for oxygen; but we have not called them that because most people have been considering the oxidation of dyes and not the reduction of oxygen.

8. Carey Lea's criticisms of Vogel's theory are based chiefly on misconceptions, but probably in part on the use of unknown dye mixtures.

Cornell University.

THE ADSORPTION OF ORGANIC MATERIALS TO THE SILVER HALIDES*

BY S. E. SHEPPARD, R. H. LAMBERT AND R. L. KEENAN

Introduction

Adsorption at liquid-solid interfaces has been studied[1] for many years. The mechanism is fundamentally more complex than at gas-solid interfaces because of adsorbent, solution, and adsorbed material of the system. Still other factors enter when a crystalline adsorbent is considered as compared with amorphous material.

The effects of adsorption in the preparation of photographic silver halide emulsions are in evidence at many stages of the process. The size and distribution of grains is affected by common ion action[2] and by concentration of gelatin.[3] The shape of grains can be altered enormously by foreign materials such as urea, dyes, etc.[4]

In the photographic emulsion adsorption of gelatin has a protective effect with respect to reduction of the silver halide apart from its effect on size-distribution, and shape. Reinders and Nieuwenburg[5] found that reduction of silver chloride by ferrous citrate was distinctly restrained by a gelatin concentration as low as 0.0012 per cent of the total system. Sheppard suggests[4] that specific orientation of active groups to silver halide surfaces may account for this protective colloid property.

A further adsorption effect is the general sensitizing imparted by gelatin to the silver halide grain. Gelatin contains certain organic sulfur-containing bodies which, on coming in contact with silver halide surfaces, react to form complex compounds which are more or less unstable. These decompose to form silver sulfide nuclei which in turn act as sensitivity centers for developing the latent image produced by light.[6] This sensitizing, so fundamental for photographic emulsion preparation, is necessarily controlled by adsorptive forces acting at the solid-liquid interface.

An integral part of photographic emulsion is optical or color sensitizing by adsorption of dyes. A considerable study has been made of the mechanism of dye deposition on crystalline material.[7] Adsorption of dyes depends on the basic or acidic nature of the dye and on the polarity of the surface of adsorbent.[8] The nature of the dispersity of dyes and the effect of concentration in solution on dispersity are still little known in most cases.

Finally, adsorption plays a primary role in the formation and development of the latent image.[9] Adsorption at silver halide surfaces must undoubtedly have an enormous influence on the free energy available for crystal growth, as described by Kossel.[10]

Adsorption of Inorganic Ions to the Silver Halides

A summary of previous work on the adsorption of materials by the silver halides is given by Wulff and Seidl.[11] The study made by Fajans[12] and co-workers in which inorganic ions were adsorbed gives evidence that photo-chemical decomposition is greatly influenced by common ion adsorption. Fajans' observation that every fourth to tenth atom of bromine in the silver bromide lattice has adsorbed a silver ion from a silver nitrate solution cannot be regarded as the same for other silver salts in solution since Beekley and Taylor[13] find that adsorption of silver ion is dependent on the anion and roughly, that the greater the solubility of silver salt the less adsorption results. Extraneous electrolytes, furthermore, have a pronounced effect on the adsorption process.

Fajans[14] describes adsorption as a dehydration of the deposited ion, thus causing a definite energy change in the silver halide lattice. He also obtained evidence of anion deformation by non-noble metal cations, thus giving polarization to the surface layer of the crystalline adsorbent.

Others have studied adsorption of inorganic salts to the silver halides, among whom are Luther[15] (cuprous ions on silver bromide), Lottermoser (common ion), and Paneth, (radium on silver chloride). The latter found no adsorption in accordance with his rule. Fajans and co-workers found adsorption of thorium B to silver halide sols stabilized by halide ions but none when stabilized by silver ions. Adsorption of thallium ions was studied by Wulff and Seidl.[11]

Adsorption of Dyes to the Silver Halides

Only a few experiments have been made quantitatively on the adsorption of dyes to the silver halides and yet this question is of paramount importance for optical and chemical sensitizing or desensitizing. Probably the first systematic study was that by Kieser.[7] Some of his conclusions will be discussed later. Others in this field were Fajans[8] and co-workers, Lüppo-Cramer,[16] Wulff and Seidl,[11] and Sheppard and Crouch.[17]

Gelatin Adsorption to the Silver Halides

Eder[18] was the first to observe definite retention of gelatin by silver halides. He reported 0.5 per cent gelatin was still retained after repeated centrifugations and washings with hot water. Reinders[14] reported 0.1 per cent adsorbed where ammoniacal silver chloride was the adsorbent. No other data could be gleaned from the literature.

Adsorption of Substances which form Compounds with the Silver Halides

Little seems known of an adsorption phase in the case of solutes forming definite addition compounds with the adsorbent (solid).

In the silver halides, one can refer to the researches of Kieser on adsorption of dyes which form slightly soluble compounds with the cation of the adsorbent. Kieser recognizes a form of adsorption in which the law of mass action is

supposed to hold.   For example, silver iodide with tetra-iodo-fluorescein gives very little intensity, while silver chloride adsorbs so strongly that quantitative results can be easily obtained.   With sodium fluoresceinate and silver halides, the solubility of the silver fluoresceinate was so high that no adsorption could be measured.

We have made some experiments in the case of allyl-thiourea and silver bromide.   These form a double compound (1:1)

$$AgBr : C-S \begin{array}{c} \diagup NHC_3H_5 \\ \diagdown NH_2 \end{array}$$
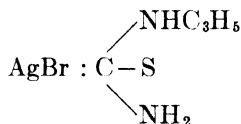
of low solubility (2.3×10^{-4} gm. mols. per liter at $25°$ C., *cf.* Sheppard and Hudson[20]) and probably also 1:2 and 1:3 compounds of much higher solubility, since high concentrations of allyl-thiourea "fix" or dissolve silver bromide. We were interested in seeing whether up to 1:1 equivalent of allyl-thiourea would be completely taken up by solid silver bromide.   This did not appear to be the case, at least, in a reasonable time.   Instead, considerably below molecular equivalence, the silver bromide grains became agglutinated, a plastic mass forming.   Apparently before the whole grain of silver bromide is converted to the 1:1 compound, the outer layer of this is carried up to the higher order compounds, and some is dissolved, since appreciable silver was found in the solution.

Experimental Results

The experiments to be recorded are preliminary to a more extensive investigation of adsorption as related to the photographic process.   In this, the adsorption of sensitizing dyes is of great importance.

An example of one such experiment is shown in Fig. 1. Pinacyanol and orthochrome T are compared under somewhat similar conditions.

The formulas and molecular weight are:

Pinacyanol   Orthochrome T

Mol. wt. 388   Mol. wt. 436
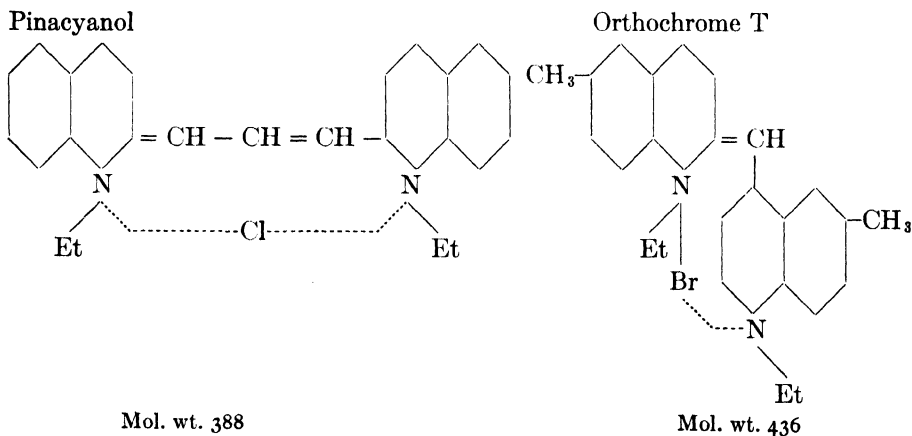
They are both basic dyes in which the dye molecules serve as cation, and halogen atoms as anion.

Sheppard and Crouch found that simple extraction with chloroform gave good quantitative data for orthochrome T dye adsorption to grains. A check was possible since final dye concentration could be obtained by centrifuging the grains and removing a portion of the solution for dye estimation.

In the case of pinacyanol an added difficulty arose since the coefficient of distribution between chloroform and water is 0.20 at pH 6.0 to 7.0, while for orthochrome T, 5.0 was found by Sheppard and Crouch at about the same pH. We found the ratio for pinacyanol could be raised by salting out with sodium chloride, the best result being obtained at 25 gm. sodium chloride per 100 c.c. dye solution. At this salt concentration 85 per cent of dye passed into the chloroform layer whose volume was fixed at 25 c.c. This partition was independent of dye concentration within the limits studied.

Furthermore, since sodium thiosulfate was used to dissolve the grains after separation from the dye solution, a study was made of the ratio of sodium chloride and sodium thiosulfate in the dye solution. It was found that if 10 gm. of sodium chloride were replaced by an equal amount of sodium thiosulfate, the same distribution coefficient was obtained as if only sodium chloride was present.

The silver bromide grains were prepared in an amount sufficient for the whole series of experiments. They were precipitated in solution of gelatin in an excess of potassium bromide present throughout. After two washings on the centrifuge, a definite amount of gelatin still adhered to the grains, of which more will be said later. This amount is equivalent to 4 mg. gelatin per gram silver bromide. A sample was taken for photomicrographic grain size determination.

Samples of silver bromide (0.34 gm.) were taken up in 100 c.c. of dye solution. The whole was well shaken mechanically for several hours at 25° C. after which the grains were separated by centrifuging. As much as possible of the dye solution was removed without disturbing the deposited grains, and its volume was accurately determined. Its concentration was determined colorimetrically.

The grains were then treated with sodium thiosulfate and sodium chloride, as described above, and the amount of dye again determined colorimetrically. Accurate results were found only for dye determination on grains since the concentration in solution was invariably low. The values obtained were erratic owing to surface adsorption to the walls of the container. Much of this error could be eliminated by coating the interior of the bottles with a rather thick layer of paraffin.

Sheppard and Crouch[17] calculated that one dye molecule was held for 2.3 bromide ions of the surface. This calculation necessarily assumes a certain state of the surface of the grains. Further, it assumed only projective area ($\times$ 2) for the adsorbing area. From photomicrographs and certain assumptions, we now consider that *three* figures can be obtained for the ratio of dye molecule adsorbed to bromide ion: (1) One may assume adsorption to the octahedral face only, that is, to the projective surface and its opposite surface; (2) total surface may be obtained if the thickness of grains is known

and a definite shape is assumed as for example a thin disk; (3) if the edges are assumed to be cubic faces, then only half the silver bromide ions on the surface could be bromine ions and a third figure would be obtained. Calculating in this way one gets respectively the numbers 1.69, 2.78, and 2.24 for bromide ions per one dye molecule adsorbed in the case of pinacyanol (Fig. 1).

The value 1.69 for octahedral adsorption is still far from unity, that is, monomolecular adsorption. This might, however, be accounted for by assuming that not all projective area is that of octahedral faces. This result may be compared (Table I) to the collected table of data taken from the paper by Wulff and Seidl.
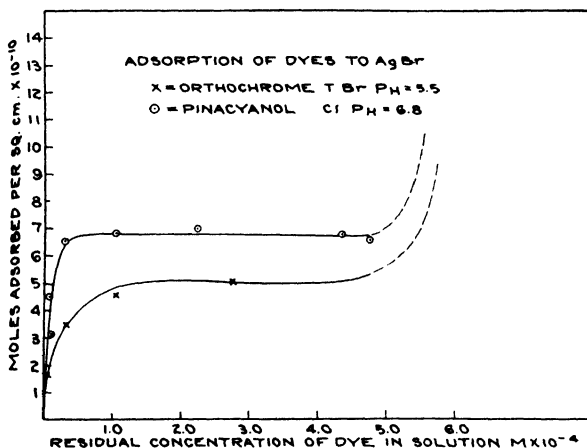
FIG. 1

It is observed that less than one molecule of material is adsorbed per ion of adsorbent. In the case of a large dye molecule such as those of the carbocyanines or isocyanines it is conceivable that there is scarcely room for an ion-to-ion union since the cross section of the quinoline group of the dye is itself as large or larger than the interionic distances of the silver bromide lattice, that is, about 6 Å, and there are two such quinoline groups per molecule of dye. Silver ion adsorption, however, could conceivably be equal to that of bromide ion on the silver bromide crystal surface. Fajans did not find this to be the case and Beekley and Taylor find that silver ion adsorption varies for various soluble silver salts.

That adsorption is dependent on electrolyte concentration and especially common ion concentration has been pointed out many times. Fig. 2 gives such an instance as observed by Wulff and Seidl[11] for the adsorption of *resorcin* to silver bromide. Silver ion increases the adsorption of this and bromine ion decreases the adsorption. Cases are shown where certain electrolytes have no effect on dye adsorption. The salts indicating no effect on adsorption in Fig. 2 are phosphates, borates and carbonates.

The effect of hydrogen ion concentration depends on the acidic or basic nature of the dye. In Table II are shown qualitative results of adsorption for

TABLE I*

Vergleich der Besetzungsdichten bei Ionenadsorption und
Farbstoffionenadsorption

Adsorbens	Adsorbat	Zahl der Ionen des Adsorbates / Zahl der adsorbierenden Ionen des Adsorbens	Autor und Bemerkungen
AgBr-Präparat III	Methylenblau in neutraler Lösung bei Sättingung der Oberfläche	1:8	⎫
,,	Tl$^+$ in n/10-NaOH bei Sättigung der Oberfläche	1:3	⎬ Diese Arbeit
,,	Resorcinat in n/10-NaOH		⎪
	0.05 M/L = 0.55%	1:1.7	⎫ Interpoliert
	0.025 ,, = 0.28%	1:2.5	⎬ aus der Adsorptions-Kurve 10 d.
	0.01 ,, = 0.11%	1:6	⎭ Fig. 3
PbSO$_4$	Ponceau 2 R bei Sättigung	1:11	⎫
PbS	,,	1:5.0	⎬ Umgerechnete Werte nach F. Paneth [35]
,,	Methylenbl. B extra bei Sättigung	1:5.5	⎬ Radio-Elements as Indikators 1928, S. 71
,,	Methylblau HB bei Sättigung	1:3.5	⎭
AgBr	Orothochrom T	1:2.3	S. E. Sheppard u. H. Crouch[34]
,,	Erythrosin	1:3	O. J. Walker[5]
,,	Ag$^+$	1:6	K. Fajans u. W. Frankenburger[1]

* From Wulff and Seidl: Z. wiss. Phot., **28**, 239 (1930).

pinacyanol, a basic dye, and for dichlorofluorescein, an acid dye, with excess common ion in alkaline and acid solution.

It is rather remarkable that pinacyanol, a basic dye, tends to adsorb in an acid medium and in the presence of Ag^+. If, however, a study of silver ion complex is made, Fig. 3, it will be observed that such complexes do occur with the basic dye as well as with an acid dye such as erythrosine.[21]

The method is essentially an electrometric estimation of Ag in the presence of dye by means of a concentration cell. The deviation from zero denotes the amount of complex ion formation.* The curves for the two dyes are not comparable since the concentrations are not the same.†
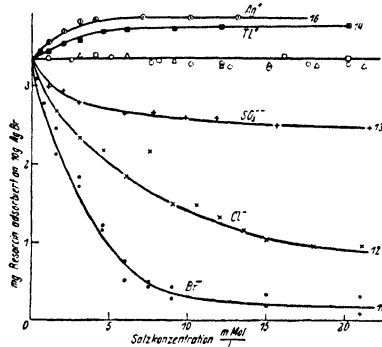
FIG. 2

From Wulff and Seidl: Z. wiss. Phot., **28**, 239, (1930).

TABLE II

Influence of pH and Common Ion Excess on Dye Adsorption

	pH	Excess Br⁻	Excess Ag⁺
Pinacyanol	5.0	+	+ +
(Basic Dye)	7.5	+ +	−
Dichlorofluorescein	5.0	−	+ +
(Acid dye)	7.5	−	+

Since silver ion complexes do form with some basic dyes it can be seen that adsorption is possible for dye on silver halide in the presence of excess Ag^+.

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* The technique and data for this are to be published by Dr. W. Vanselow and one of us later.

† There is, however, another factor to be kept in mind. The pinacynanol studied was a chloride derivative, and accordingly, silver ion might combine chemically with the chloride of the dye. The result would depend on the solubility of AgCl as compared with silver dye compound. The solubility product of AgCl is taken as 1.56×10^{-10} at 25°C. Then, knowing the concentration of chloride ion which is assumed to be equal to the dye concentration for the total ionization of dye chloride, one can calculate the Ag^+ concentration. For dye concentration of 1:40,000 this is found to be 2.5×10^{-6}. The observed Ag^+ concentration was approximately 3.0×10^{-7}, i. e., the observed Ag^+ concentration is about 0.1 that of the amount calculated.

This could be accounted for if as much as 1% of the dye halide was found to be bromide. Qualitatively, no trace of bromide was observed in the dye.
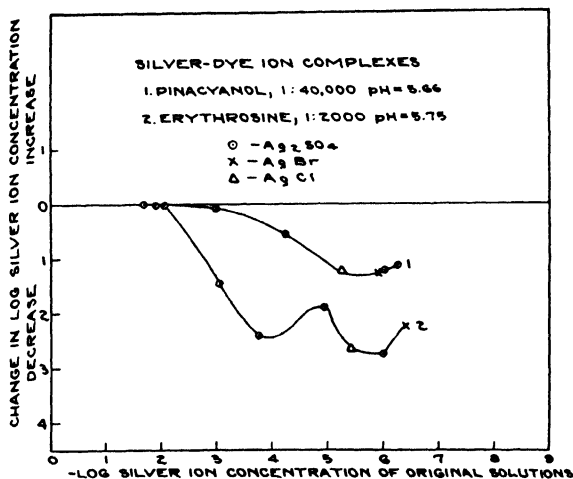
FIG. 3

Adsorption of Gelatin to Silver Bromide

In the first experiment a sample of silver bromide of known grain size distribution was prepared in gelatin solution by adding silver nitrate to potassium bromide in the presence of excess of the latter. A short after-ripening was given and the grains were removed from the solution by centrifuging.

The grains were taken up by distilled water at 50°C. and recentrifuged. This was repeated four times, but before each repetition a sample was removed for nitrogen determination. A repeat was run as a check. The nitrogen was determined, as described by Parnas and Wagner,[22] by a micro-Kjeldahl method, the conversion factor of 5.6 being used for obtaining gelatin. The conclusion drawn is that after two washings no more nitrogen and therefore presumably gelatin can be removed (Table III).

TABLE III

Effect of Washing on Gelatin adsorbed to Silver Bromide Grains

Times Washed	pH Washing	mgms. Nitrogen per gm. Silver Bromide	mgms. Gelatin per gm. Silver Bromide
1	6.5	—	—
2	6.5	0.60	3.38
3	6.5	.61	3.40
4	6.5	.59	3.36

The effect of pH was next tried. In this case two washings were made with four different buffer mixtures. Table IV indicates slight decrease in adsorption only in acid medium. The value is, however, almost within the experimental error. pH then does not affect this phenomenon.

TABLE IV

Effect of pH on Gelatin adsorbed to Silver Bromide Grains

Sample	pH of Buffer	mgms. Nitrogen per gm. Silver Bromide	mgms. Gelatin per gm. Silver Bromide
1	4.0	0.57	3.19
2	6.0	.691	3.87
3	8.0	.632	3.54
4	10.0	.686	3.85

FIG. 4

Silver Bromide Grains from Gelatin Solution refluxed 6 hours

Since the areas of these grains have been determined by the photomicrographic method it is possible to calculate the thickness of gelatin layer assuming adsorption to the grain surface. Using the data obtained by two of us[23] for gelatin films on mercury the thickness found on these grains would correspond to a double layer of gelatin molecules.

On the other hand, it was later shown that about one-half of this gelatin could be removed by digesting with boiling water. This might imply that a monomolecular layer was actually present and that the rest of the gelatin was occluded in the grain; or, it is possible that a secondary layer is attached to the primary layer by weaker forces.

An experiment was next tried to determine whether all the gelatin could be removed, provided drastic means were taken. One sample of grains after the two washings was subjected to distilled water at 100°C., and another to 10 per cent sulfuric acid at its boiling point. The two were digested six hours. A motor-driven stirrer kept the grains in suspension during the operation. Photomicrographs (Fig. 4) of the resulting sample show little effect on shape or dispersion of the grains treated in distilled water, although profound changes occurred in the highly acidified solution.

On determining the nitrogen content only about one-half the gelatin retained on centrifuging and washing was present in the first case and less than one-tenth in the second. Further experiments are planned on the conditions of removal of gelatin from silver halide. The fact is clear in any case that some nitrogeneous material is tenaciously held to the grain (Table V).

TABLE V
Removal of Gelatin from Silver Bromide by hydrolyzing with (a) Water and (b) Sulfuric Acid

	1st Trial		2nd Trial	
Solution	mgms. Nitrogen per gm. Silver Bromide	mgms. Gelatin per gm. Silver Bromide	mgms. Nitrogen per gm. Silver Bromide	mgms. Gelatin per gm. Silver Bromide
Distilled Water	0.22	1.23	0.273	1.53
Sulfuric Acid	0.061	0.34	.056	0.31

Finally, the effect of heat treatment of grains in 5 per cent gelatin solution has within limits shown no influence on adsorption. That is, raising the temperature from 40°C. to 60°C. and holding at either temperature for several hours does not affect the amount of adsorption.

A further experiment was now tried of adding silver bromide prepared without gelatin to various concentrations of gelatin solution. The silver bromide was prepared by adding silver nitrate to potassium bromide solution in the same manner for each sample. In Table VI the fourth sample was contaminated with 4 per cent nitric acid immediately after precipitation.

TABLE VI
Adsorption of Gelatin to 5 gm. AgBr precipitated without Gelatin

Sample	Mg. Gelatin on Grains	Mg. Gelatin in soln.	Sample	Mg. Gelatin on Grains	Mg. Gelatin in soln.
1	4.0	11.0	4	28.9	104.0
	4.3	10.7		32.0	101.0
2	13.0	18.0	5	22.2	179.0
	14.2	16.5		23.9	178.0
3	14.0	53.0			
	15.9	52.0			

The sample, however, was washed with distilled water exactly as for the other samples. The higher adsorption value is presumably due to a higher total surface of grains, since little time was available for grain ripening as compared with that of the other samples. Checks were run at each gelatin concentration.

Summary

(1) The adsorption of pinacyanol, a basic dye, to silver bromide has been studied at pH = 6.8. Calculation of dye adsorbed to Br^- of the octahedral surface shows that 1.69 Br^- is necessary for one dye molecule. Calculations

are also made of total surface assuming both cubic and octahedral faces of silver bromide.

(2)   Qualitatively it is shown that an acid dye such as dichlorofluorescein adsorbs to AgBr only for excess Ag^+ and mainly in an acid medium. Pinacyanol adsorbs mainly in alkaline medium and for an excess of Br^-.

(3)   Although allyl-thiourea does not follow any adsorption formula in its addition to the silver halides, the nature of the substances formed and the solubility of the various compounds is such that in some cases the reaction may not go on to completion.

(4)   Gelatin is found to adsorb to silver bromide and when the halide is prepared in the presence of gelatin a layer of gelatin about the grain is so formed that it cannot be removed by boiling with water for many hours. Ten per cent sulfuric acid does not remove all the adsorbed material even after six hours' digestion, although the grains are markedly altered. Enough gelatin is still present after water digestion to amount to a monomolecular layer about the grain.

Bibliography

[1] Freundlich: "Colloid and Capillary Chemistry," (1926); A. Taylor: "Treatise on Physical Chemistry," 2nd Ed. (1924).

[2] S. E. Sheppard and R. H. Lambert: Flocculation and Deflocculation of the Silver Halides, Colloid Symposium Monograph, 4, 281, (1926); Grain Growth in Silver Halide Precipitates, 6, 265 (1928).

[3] A. P. H. Trivelli and S. E. Sheppard: "The Silver Bromide Grain of Photographic Emulsions," Monograph No. 1, from the Kodak Research Laboratories (1921).

[4] S. E. Sheppard: The Function of Gelatin in Photographic Emulsions, Phot. J., 69, 331 (1929).

[5] W. Reinders and C. J. Nieuwenberg: Kolloid-Z., 10, 36 (1921).

[6] S. E. Sheppard: Photographic Sensitivity: A Colloid Chemical Problem, Colloid Symposium Monograph, 3, 76 (1925).

[7] K. Kieser: Beiträge zur Chemie der optischen Sensibilization von Silbersalzen, Dissertation, Freiburg (1904).

[8] K. Fajans, et al: Z. Elektrochemie, 34, 502 (1928).

[9] S. E. Sheppard: Die Silberkeimtheorie der Entwickelung, Phot. Korr., 59, 76 (1922).

[10] W. Kossel: Die molekulären Vorgänge beim Krystallwachstum, in Falkenhagen's "Quantentheorie und Chemie" (1928).

[11] P. Wulff and K. Seidl: Adsorption als Primärvorgang der photographischen Entwickelung, Z. wiss. Phot., 28, 239 (1930).

[12] Discussed by H. B. Weiser: "The Colloidal Salts" (1928).

[13] J. S. Beekley and H. S. Taylor: The Adsorption of Silver Salts by Silver Iodide, J. Phys. Chem., 29, 942 (1925).

[14] Loc. cit.

[15] Discussed by H. B. Weiser: "The Colloidal Salts," 217-219 (1928).

[16] Eder's Handbuch: Die Grundlagen der photographischen Negativverfahren, 2. I; (1927).

[17] S. E. Sheppard and H. Crouch: The Optical Sensitizing of Silver Halide Emulsions, I. The Adsorption of Orthochrome T to Silver Bromide, J. Phys. Chem., 32, 751 (1928).

[18] J. M. Eder: Sitzungsber. k.-k. Akad. Wiss. Wien, 90 II, 1097 (1884).

[19] W. Reinders: Z. physik. Chem., 77, 687 (1911).

[20] S. E. Sheppard and J. H. Hudson: Addition Compounds of Allylthiourea, J. Am. Chem. Soc., 49, 1814 (1927).

[21] S. E. Sheppard: Antifogging and Antisensitizing Compounds (Correspondence), Phot. J., 70, 439 (1930).

[22] F. Pregl: "Quantitative Organic Microanalysis" (1924).

[23] S. E. Sheppard, A. H. Nietz and R. L. Keenan: Supermolecular State of Polymerized Substances in Relation to Thin Films and Interfaces, Ind. Eng. Chem., 21, 126 (1929).

THE PRECIPITATION OF PROTEINS IN PACKING HOUSE WASTES BY SUPER-CHLORINATION

BY H. O. HALVORSON, A. R. CADE* AND W. J. FULLEN**

With the present increasing agitation against stream pollution, civic organizations, municipalities, and industries are more than ever faced with the problem of satisfactorily treating industrial wastes. Unfortunately, the biological methods that have been so successful for domestic sewage are not always applicable. The high strength of these wastes frequently makes the cost of these methods entirely excessive, and the chemicals present often interfere with biological activity. Even when it is possible to mix the two the results are frequently unsatisfactory. In facing this problem, sanitary engineers are therefore being forced to reconsider the almost discarded chemical precipitation method of sewage treatment.

Geo. A. Hormel & Co., packers at Austin, Minnesota, early arrived at the decision that biological methods were out of the question, and instituted a program of research to find the method of chemical precipitation most applicable to their waste. In this connection, some of the underlying fundamentals have been investigated at the Department of Bacteriology, University of Minnesota, and at their own laboratories in Austin.

In order to relieve pollution in the Cedar river as much as possible, the Hormel company, several years ago, provided for preliminary treatment such as the removal of the paunch manure by suitable screening, and the removal of easily settleable solids by primary sedimentation. Waste from the stock yards was collected and used as fertilizer on neighboring farms, and domestic sewage coming from the plant was put directly into the city sewers. These modifications, however, did not materially relieve pollution in the river. The by-passing of all condenser and other clean water served to reduce the volume of the sewage in preparation for chemical treatment. With these provisions, the Cedar river received about three-fourths million gallons of packing house waste that contained approximately 2500 parts per million of volatile solids and that had a B.O.D. of about 1800. From 75 to 80% of these solids were in colloidal suspension and could not be removed by further sedimentation. The balance appeared to be in true solution. The object of the investigation was to find ways and means of removing all of the former and as much of the latter as possible.

Various methods of chemical precipitation as a means of sewage clarification have been studied in the past, but none of them have been extensively applied in this country. In this connection there are various principles that

may be employed. The proteins may be precipitated by adjusting the pH to the isoelectric point, such as in the Miles Acid Process,[1] or they may be precipitated by neutralizing the charge with the salts of various metals, such as iron or aluminum. It may be argued that this is not exactly a charge neutralization, but that the protein salts of the heavy metals are formed. This is being investigated at this time, but results are not as yet ready for publication. Proteins may also be precipitated by denaturing them with oxidizing agents or other coagulants.

The Miles Acid Process was eliminated because good results can be obtained only in case the pH is very accurately controlled. This cannot be accomplished by manual methods in a plant that operates on a continuous flow, and since no fool-proof automatic methods have as yet been devised, it was felt that this process could not be relied upon for uniformly good results. Likewise, coagulation with aluminum or iron salts was rejected because it was felt that with manual control it would be difficult to avoid excessive ash content in the recovered product. Of the coagulants in the third class, chlorine appeared to be the most promising from an economic standpoint. That this chemical could be used for the precipitation of proteins was pointed out as early as 1840 by Mulder,[2] Thenard,[3] Berzelius,[4] and DeVrij.[5] In 1897 Rideal and Stewart[6] advocated the use of chlorine for the precipitation and quantitative determination of gelatin and peptone in meat extracts. The authors stated that the precipitate so obtained flocced and filtered readily and was quantitatively weighable. According to them, the percentage of gelatin found by this method checked very closely with that found by any other then in use. They also noted that the proper drying of the precipitate was an important factor, since at high temperatures the precipitate decomposed and became discolored. Their precipitation was accomplished by bubbling chlorine gas through the solution until coagulation was complete. It is apparent from this that they were using very large quantities of chlorine. In an article published in 1910 Rideal again points out that the chlorine will completely precipitate all proteins and peptones, but that it does not throw down the amino acid or organic bases even though it does combine with them. There is no indication in the literature that Rideal ever attempted to make use of this in a practical way for the treatment of sewage, although he does mention in his publication of 1910 that clarification observed when small amounts of chlorine were added to sewage might be due to this precipitation. This is in contradiction to his statement that when small quantities of chlorine are added, soluble compounds of the proteins are formed.

[1] U. S. Patent, 1,134,280. April 6, 1915.

[2] Berzelius Jahresber., **19**, 734 (1840); Jahresber. Chem., **44**, 489 (1848).

[3] Mém. d'Arcueil, **2**, 38. Quoted by Rideal.

[4] Jahresber., **19**, 729 (1840).

[5] Ann. Pharm., **61**, 288 (1847).

[6] Analyst, **22**, 228 (1897).

A great deal of work has been reported in the literature[7] on the reaction of chlorine with proteins and protein products in connection with antiseptic studies. To the best of our knowledge, however, none of these references call attention to the protein-precipitating power of this element, and none of the investigators attempted to make any practical use of this property of chlorine. In fact, the reports in the literature would lead one to believe that the amounts of chlorine required are too excessive for any such purpose.

Our data show that native proteins are precipitated by comparatively small amounts of chlorine, while modified proteins such as gelatin require larger quantities, and peptones are precipitated only when very high concentrations are used. Our work confirms that of Rideal and other early investigators in showing that amino acids are not precipitated, although they may be reacted upon and sometimes decomposed by the chlorine. Our data also show that precipitation can be effected even in solutions that contain mixtures of various proteins and their decomposition products, although in such cases sufficient chlorine must be added to satisfy in part the demands of all the compounds present. In the following tables may be found the effects produced when the chlorine is added to pure solutions of various proteins and their decomposition products, as well as solutions containing mixtures of the two. The quantities of chlorine indicated in these data are approximately the minimum amounts required for the precipitation.

TABLE I

Effect of Chlorine on Various Proteins and Protein Derivatives

Substance	Nitrogen Grams per 100 cc	Chlorine Grams per 100 cc	Cl/N ratio	Remarks
Egg albumin	0.0096	0.0202	2.1	Precipitation-filtrate clear
Fresh blood	0.0096	0.0240	2.5	Precipitation-filtrate clear
Gelatin	0.0096	0.0403	4.2	No precipitate-filtrate milky
Gelatin	0.0096	0.0500	5.1	Partial precipitate-filtrate milky
Peptone	0.0096	0.0580	6.1	No precipitation
Peptone	0.0096	0.1530	16.0	No precipitation
Peptone	0.0096	0.3500	36.4	No precipitation-filtrate milky
Tryptophane	0.0096	—	—	No precipitation-filtrate red
Tryptophane	0.0096	0.1200	12.5	Precipitation-filtrate dark red
Glycine	0.0096	0.1920	20.0	No precipitation

[7] Chattaway: Trans. Chem. Soc., **87**, 145 (1905); **107**, 1814 (1915); Dakin: Brit. Med. J. Aug. 28, Oct. 23, Nov. 27, Dec. 4, 1915; (1) 852 (1916); Dakin, Cohen, Daufresne, and Kenyon: Proc. Roy. Soc., **89 B**, 232 (1916); Dakin and Dunham: "Handbook on Antiseptics," (1917); Raper, Thompson and Cohen: J. Chem. Soc., **85**, 371 (1904); Rideal; J. Roy. Sanit. Inst., **31**, 33 (1910); Rideal and Rideal: "Chemical Disinfection and Sterilization" (1921); Smith, Drennan, Rettie and Campbell: Brit. Med. J., (2) 129 (1915); Taylor and Austin: J. Exp. Med., **27**, 155 (1899); Tilley: J. Agr. Res., **20**, 85 (1920); Tilley and Chapin: J. Bact., **19**, 295 (1930); Tonney and Greer: Am. J. Publ. Hlth., **18**, 1259 (1928); Tonney, Greer and Liebig: Am. J. Publ. Hlth., **20**, 503 (1930).

TABLE II

Effect of Chlorine on Mixtures of Proteins and Their Decomposition Products

Substances		Nitrogen Grams per 100 cc.		Chlorine Grams per 100 cc	Cl/N ratio
A	B	A	B		
Albumin	Tryptophane	0.0074	0.0000	0.0145	2.0
,,	,,	0.0070	0.0005	0.0240	3.2
,,	,,	0.0059	0.0020	0.0476	6.0
,,	,,	0.0037	0.0048	0.0817	9.6
,,	Glycine	0.0074	0.0005	0.0215	2.8
,,	,,	0.0037	0.0048	0.0560	6.6
,,	Peptone	0.0070	0.0005	0.0215	2.8
,,	,,	0.0037	0.0048	0.0301	3.5
,,	Gelatin	0.0055	0.0024	0.0173	2.2
,,	,,	0.0037	0.0048	0.0173	2.1
Blood	,,	0.0120	0.0048	0.0522	3.2
,,	,,	0.0180	0.0024	0.0522	2.5

It is to be observed that in the case of pure protein solutions, precipitation can be effected by comparatively small amounts of chlorine. The chlorine requirement is increased somewhat in the presence of peptones, but considerably more in the presence of amino acids, while gelatin increases the demand less than either of the former. Thus albumin and blood proteins are precipitated when the Cl/N ratio is 2.5 or less, whereas a ratio of 6.0 or above is required when amino acids are present. Since the Cl/N ratio is calculated from the total nitrogen present, it is apparent that nitrogen compounds which are not precipitated will lower the efficiency of the process to an even greater extent than is indicated by the ratios given in the above table. Table III further emphasizes this fact by showing that the percentage removal decreases materially when amino acids or peptones are present.

TABLE III

The Percentage Removal of Nitrogen by Chlorine Precipitation
of Various Organic Nitrogen Mixtures

Substance		Concentration Gms N per 100 cc		Grams N in precipitate	Percentage removal
A	B	A	B		
Albumin		0.0418		0.0417	99.7
Albumin	Gelatin	0.0208	0.0272	0.0441	91.8
Albumin	Blood	0.0208	0.0105	0.0303	96.8
Albumin	Tryptophane	0.0208	0.0099	0.0220	71.6
Albumin	Peptone	0.0208	0.0254	0.0209	45.2

In the case of mixtures of gelatin and protein, it appears that the gelatin is precipitated even though the Cl/N ratio is less than that ordinarily required to precipitate it alone. Thus we see that in Table III where a nitrogen

removal of 91.8 is obtained, a considerable portion of the nitrogen must have come from the gelatin. The flocculent precipitate formed by the native proteins apparently occludes the fine colloidal precipitate formed from the gelatin, so that a clear filtrate is produced in a mixture of this type, whereas in a pure solution of gelatin the fine precipitate will not settle out. To produce a clear filtrate with a mixture of native proteins and gelatin, it is necessary to stir the solution gently for about 10 minutes following the addition of the chlorine.

In coagulating proteins, definite ranges of chlorine concentration are required before any precipitate is formed. Small amounts of chlorine do not produce proportionate amounts of precipitate, but instead all the proteins precipitate when a definite range is reached. This is illustrated in the following table which shows the results obtained with different concentrations of egg albumin.

Table IV

The Effect of varying the Chlorine Concentration on Albumin Solutions

Concn. egg albumin	Concn. Chlorine			Cl/N ratio	
Gms. N per 100 cc.	No. pptn.	Pptn. starting	Pptn. complete	Pptn. starting	Pptn. complete
0.074	0.145	0.160	0.170	2.1	2.3
0.0074	0.016	0.0165	0.0170	2.2	2.3
0.00148	0.0029	0.0032	0.0034	2.1	2.3
0.00074	0.0012	0.0017	0.0017	1.9	2.3

The above data indicate that definite proportion of chlorine to nitrogen is needed before precipitation occurs, regardless of the concentration of the latter. This would imply that the chlorine requirements are independent of the concentration of organic matter. This has been checked by determining the minimum amount of chlorine required to produce precipitation after a reaction period of 15 minutes. The data are given in Table V.

Table V

The Effect of Concentration of Protein on the Cl/N Ratio

Concn. of Egg Albumin Gms. N in 100 cc.	Concn. of Chlorine Gms. per 100 cc. necessary for precipitation	Cl/N ratio
0.1000	0.2250	2.25
0.0500	0.1125	2.25
0.0250	0.0580	2.28
0.0200	0.0436	2.18
0.0100	0.0224	2.24
0.0050	0.0102	2.04
0.0025	0.0051	2.04
0.0011	0.0019	1.80
0.0001	No visible precipitate	

Within experimental error, it appears that the quantity of chlorine required is dependent only upon the amount of protein present and independent of its concentration. The slight decrease which occurs in the dilute solution may be due to experimental error which is difficult to avoid in those cases.

The chlorine-nitrogen ratio of from 2.0 to 2.3, which is necessary for the precipitation of proteins from pure solutions, can be lowered considerably by an adjustment of the reaction. In pure solutions the final reaction is brought to a point somewhere between pH 2.0 and 4.0, depending upon the concentration of proteins present. In reacting with the protein, the major portion of the chlorine is converted to hydrochloric acid, which causes a lowering in the pH. If some of this acid is neutralized so that the final pH is about 4.0, precipitation can be effected with considerably less chlorine. That it does not appear to make any difference which alkali is used for this purpose is indicated in the table below. The same end result is obtained whether the alkali or chlorine is added first. The amount of alkali needed depends upon the quantity of chlorine used, and since that in turn is governed by the concentration of protein present, the alkali dosage must be varied in accordance with the strength of the solution treated. In samples of waste from a packing establishment, we have found that there is usually present more than enough alkali in the form of carbonates of calcium and sodium. In those cases, then, the pH must be adjusted to 4.0 by adding a small amount of mineral acid or by adding a little excess of chlorine. The condition can be partially alleviated by preventing clean waters, which usually contain carbonates, from being mixed with the sewage. Tables VI and VII show the minimum amounts of chlorine which give a clear supernatant liquor when the reaction is adjusted to the optimum.

TABLE VI

The Effect of Various Alkalies on the Chlorine Demand
in Protein Precipitation

Concn. Protein Gms. N per cc.	Minimum gms. chlorine required to precipitate	Cl/N ratio	Comparative minimum amounts of alkali required for adjustment		
			$N/130$ CaO	$N/10$ NaOH	$N/10$ Na$_2$CO$_3$
0.0077	0.0090	1.1	20 cc.	1.4 cc.	1.4 cc.
0.0134	0.0157	1.1	35	2.5	2.7
0.0192	0.0225	1.1	50	3.7	3.6

In Table V above it was shown that for a certain range the Cl/N ratio is independent of the concentration of the protein. The same condition is true if the reaction is adjusted as shown in Table VIII.

Here, as in the unadjusted series, the Cl/N ratio appears to be independent of the amount of protein present, particularly in the more concentrated solutions. There appears to be a slight increase in the ratio in dilute solutions, although this may be due to experimental error. The percentage error will naturally be high in the solutions that contain 25 p.p.m. or less of nitrogen.

TABLE VII

The Effect of Alkali on the Chlorine Precipitation of Various Proteins

Protein	Nitrogen Grams per 100 cc	Alkali	Chlorine Grams per 100 cc	Cl/N ratio
Albumin	0.0096	None	0.0210	2.1
,,	0.0096	CaO	0.0130	1.3
Gelatin	0.0096	None	0.0420	4.2
,,	0.0096	CaO	0.0210	2.1
50-50 mixture albumin and gelatin	0.0096	None	0.0260	2.6
,, ,,	0.0096	CaO	0.0150	1.5
50-50 mixture gelatin and blood	0.0096	None	0.0310	3.2
,, ,,	0.0096	CaO	0.0100	1.0
50-50 mixture albumin and peptone	0.0096	None	0.0240	2.5
,, ,,	0.0096	CaO	0.0125	1.3
50-50 mixture blood and albumin	0.0096	None	0.0280	2.8
,, ,,	0.0096	NaOH	0.0110	1.1
,, ,,	0.0096	CaO	0.0110	1.1
Blood	0.0096	NaOH	0.0105	1.1
,,	0.0096	None	0.0270	2.8
⅓ each albumin, blood and peptone	0.0096	None	0.0480	5.0
,, ,,	0.0096	CaO	0.0270	2.7

TABLE VIII

The Effect on Chlorine Consumption of varying the Protein Concentration with an Adjusted Reaction

Concn. Egg Albumin Gms. N per 100 cc.	Concn. Chlorine necessary for precipitation Grams per 100 cc.	Cl/N ratio
0.1000	0.1170	1.17
0.0500	0.0560	1.12
0.0250	0.0285	1.14
0.0200	0.0218	1.09
0.0100	0.0109	1.09
0.0050	0.0057	1.14
0.0025	0.0031	1.24
0.0010	0.0014	1.40
0.0001	No visible precipitate	

Since the Cl/N ratio is constant in solutions containing 100 p.p.m. or more of nitrogen, it is possible to predict the nature of the curve that would be obtained if this ratio were plotted against protein concentrations. This is illustrated in Fig. 1. The solid lines are plotted from the experimental data given in Tables VII and VIII. The dotted lines are predicted. It is assumed that with concentrations above 0.1000 the Cl/N ratio will remain constant. Since the amount of HCl generated decreases with a decrease in nitrogen content, the amount formed when the solution contains less than 25 p.p.m. of nitrogen will be only slightly greater than that required to adjust
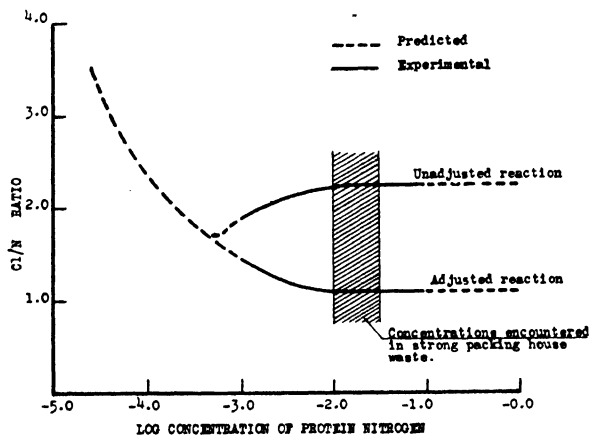
FIG. 1

Effect of Chlorine Concentration on The Chlorine-Nitrogen Ratio

the reaction to its optimum. Since conditions are then more favorable for precipitation, less chlorine should be required. This accounts for the drop in the curve for the unadjusted reaction. This tendency will continue until the chlorine added is the exact amount for the pH adjustment. After that, additional chlorine must be used to acidify the solution, and the Cl/N ratio will naturally increase.

As the reactions in the unadjusted solutions approach the optimum, less alkali will be needed to neutralize the excess acid formed, until finally none at all will be needed. At this point, then, no saving in chlorine will be effected by the addition of alkali, and the two curves will meet. Since the points in the above curve that show deviations from a straight line occur with dilute solutions in which experimental errors are large, the entire curve should be regarded as theoretical until verified by more rigid experimental data. The shaded area shown in Fig. 1 represents nitrogen concentrations of between 100 and 300 p.p.m., which strength can be easily obtained in packing plant wastes. In this range the Cl/N ratio is independent of strength. If the strength is reduced below 100 p.p.m. of nitrogen, the ratio for the adjusted series increases with increasing dilution. Since normal packing house sewage usually contains an excess of alkali, this is the curve which will normally be followed. In case there should be no alkali present, it will be desirable, from

the standpoint of economy, to add some. The adjusted curve shows the desirability of concentrating the sewage to a point where it will contain 100 p.p.m. or more of organic nitrogen. This is generally accomplished by by-passing the clean water coming from the plant. Since such waters contain bicarbonates of both sodium and calcium, their elimination has the additional advantage of reducing the excess alkalinity.

In addition to the optimum that exists at approximately pH 4.0, there appears to be another optimum at pH 2.0 or less, particularly with chlorinated egg albumin. Thus we find that the Cl/N ratio can be decreased to 1.0 if a comparatively large amount of H_2SO_4 is added. This range has not been
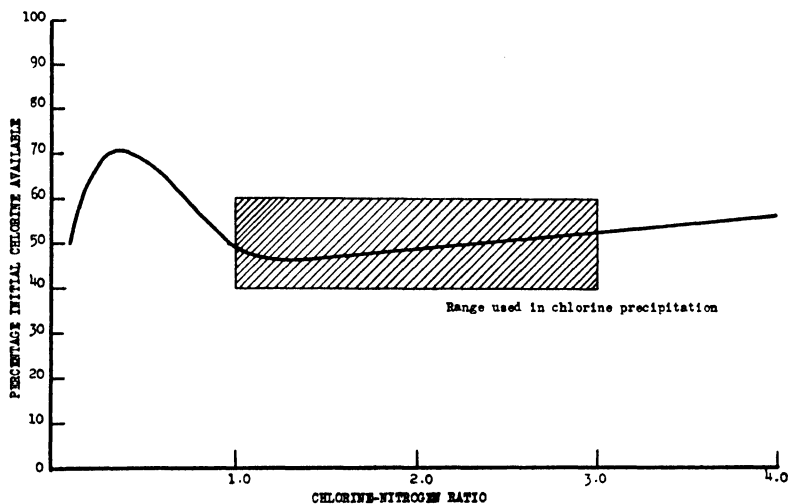
FIG. 2

Percentage of Initial Chlorine available in Various Mixtures of Chlorine and Gelatin.
(Data taken from N. C. Wright)

investigated with other proteins, since the large amount of acid necessary would counteract any saving of chlorine that could be effected. In addition, other undesirable conditions would be encountered.

In the reaction between chlorine and protein, a portion of the chlorine reacts with the amino groups to form chloramines, a portion may replace hydrogen in other parts of the molecule, some may react into double bonds, and another portion, in the form of hypochlorous acid, may react in such a way that oxygen is introduced into the molecule instead of chlorine. In this connection, and in the light of the researches of Dakin[8] and Wright,[9] our data are of particular interest.

Dakin has shown that the percentage of chlorine forming chloramines depends upon the relative amounts of protein and chlorine taking part in the reaction. This was investigated in more detail by Wright. He confirmed the

[8] Dakin: Biochem. J., 11, 79 (1917); 10, 319 (1916); Proc. Roy. Soc., 89 B, 232 (1916); Brit. Med. J., 1, 852 (1916).
[9] Wright: Biochem. J., 20, 525 (1926) and Personal Communication.

results of Dakin and was able to show graphically the amount of available chlorine present when varying quantities of proteins were added to fixed amounts of chlorine. From his data, we have been able to correlate the amount of available chlorine with the Cl/N ratio. This has been done for gelatin, and is illustrated in Fig. 2. In a private communication, Wright has presented data which show that the position and shape of the curve varies with the pH, so that the relationship shown in Fig. 2 should not be regarded as definite for all pH values.

It can be observed from this curve that when chlorine is added to a protein, a considerable amount can no longer be accounted for by thiosulphate titration. With a chlorine nitrogen ratio of from 1 to 5, as shown by the shaded area in Fig. 2, more than 50% of the chlorine is unavailable. If we assume that all of this has reacted as an oxidizing agent, it is possible, from determinations of available chlorine in the supernatant liquor and precipitate, to show the percentage that has reacted in this way. The data are presented in Table IX.

It is to be observed from these data that from 48 to 64% of the chlorine becomes unavailable when no alkali is used for the adjustment of the pH. With the alkali present, the unavailable chlorine ranges from 72 to 92%. Attempts have been made to determine the exact amount of this which has reacted in the form of hypochlorous acid with the introduction of oxygen into the protein molecule. Suggestive data have been obtained, but further work is required before definite conclusions can be drawn. By titrating with standard alkali, the total acidity has been determined. If this is calculated on the basis of HCl, we have found that its chlorine equivalent checks, within experimental error, with the unavailable chlorine plus one-half of the available. Since, when chlorine reacts with the amino groups to form chloramines, one-half of the chlorine goes to HCl, the results indicate that all of the unavailable chlorine has reacted as an oxidizing agent introducing oxygen into the protein molecule. Since the method used for determining the amount of HCl formed is not very accurate, particularly in the presence of protein buffers, it cannot be stated definitely that no chlorine is introduced into the protein molecule except that which is in the form of chloramines. It should, however, be safe to conclude that the majority of the unavailable chlorine has been converted to HCl. We have also observed that the modified proteins are precipitated at pH 4 or less as readily when the available chlorine has been removed by thiosulfate as when the chloramines are left intact. This would lead one to believe that the chlorine which has reacted as an oxidizing agent is of primary importance in modifying the proteins for the precipitation.

It is of particular interest to note that the amount of available chlorine in the supernatant liquor is very low when native proteins are the only nitrogenous compounds present, and particularly so when the reaction is adjusted. The amount increases in proportion to the concentration of nitrogenous material that is not precipitated. In the practical application, the available chlorine in the effluent ranges from 25 to 50 parts per million.

TABLE IX

Distribution of Available Chlorine in Protein Precipitation

Composition	Total N (Grams)	Available Chlorine		Gms. Cl. added	Percentage Cl. used in oxidation
		P.p.m. in effluent	Grams in ppt. from 100 cc. solution		
100 parts albumin, no alkali	.0077	.0016	.0033	.0126	61
	.0077	.0003*	.0052	.0151	64
	.0077	.0008	.0061	.0063	58
75 parts albumin 25 parts peptone, no alkali	.0077	.0047	No. ppt.	.0126	63
	.0077	.0028*	.0032	.0151	60
	.0077	.0026	.0052	.0163	48
50 parts albumin 50 parts peptone, no alkali	.0077	.0051	.0016	.0150	56
	.0077	.0048*	.0017	.0163	60
	.0077	.0047	.0029	.0201	63
25 parts albumin, 75 parts peptone, no alkali	.0077	.0066*	.0012	.0163	52
	.0077	.0066	.0016	.0201	59
	.0077	.0069	.0018	.0227	62
50 parts albumin, 50 parts peptone, with alkali	.0077	.0006	.0002	.0050	84
	.0077	.0012*	.0005	.0075	78
	.0077	.0020	.0008	.0100	72
100 parts albumin, with alkali	.0077	.0002	.0006	.0050	84
	.0077	.0002*	.0010	.0062	81
	.0077	.0002	.0013	.0075	80
Albumin with no alkali	.0192	.0012*	.0130	.0375	62
Albumin with alkali	.0192	.0000*	.0015	.0175	92
50 parts albumin 50 parts peptone, no alkali	.0192	.0124*	.0067	.0450	58
50 parts albumin 50 parts peptone, with alkali	.0192	.0025*	.0017	.0200	79

* Combinations in which the minimum amount of chlorine was used to give complete precipitation.

The above theoretical studies are of value in determining the limitations of the process. For efficient and economical chlorine precipitation, the waste must contain a comparatively large amount of native proteins, and must be treated before extensive septic action has taken place. From our experience with the waste from the plant of Geo. A. Hormel & Co., we feel that packing

house sewage can be successfully treated by chlorine precipitation. We have found that from various samples of waste from the Hormel plant, 40 to 85% of the organic nitrogen can be removed. Samples containing relatively high percentages of blood gave the higher results, whereas those that had become septic or otherwise contained large amounts of peptone or gelatin gave lower yields. Composite samples from typical runs usually showed removals of from 60-89%. The following table presents some representative results of actual plant operation.

TABLE X

Data on Plant Operation

Substance	Raw Sewage	Effluent	Percentage Reduction
	(parts per million)		
Organic nitrogen	166.84	44.0	73.0
Ammonia nitrogen	17.31	14.4	—
Total nitrogen	184.15	58.4	68.0
Total solids	4971.00	3235.0	35.0
Fixed solids	2431.00	2582.5	—
Volatile solids	2540.00	652.5	74.4
Sodium chloride	2422.00	2292.0	—

10,591 pounds of sludge obtained from 660,000 gallons.

The data reported in the above table are representative of data obtained from carefully composited samples on days when the packing plant was operating at normal capacity. The significant figures are those showing reduction in organic nitrogen and volatile solids, the former being 73% and the latter 74%. In the various analyses that have been made, these figures show a variation of from 60 to 80%.

When the plant is operating at normal capacity about 5 tons of sludge are obtained daily. The above figure of 10,591 pounds is representative. About two tons of this are obtained in a primary clarifier without chlorine precipitation, while the other three tons are obtained in a secondary clarifier following the introduction of enough chlorine to give a Cl/N ratio of from 1.3 to 1.5. The following is a representative analysis of the sludge obtained by chlorine precipitation after it has been dewatered and dried.

Moisture	3.70%
Protein	48.90%
Ammonia	9.50%
Fat	22.72%
Ash	11.60%

The engineering features and practical results of the plant, having been published elsewhere,[10,11] are not repeated here for the sake of brevity. As has been pointed out in previous publications, the cost of installation is about one-third of the estimated cost of a biological plant. The saving in depreciation and

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[10] Municipal Sanitation, April 1931.

[11] Sewage Works Journal, 3, No. 3, 488 July (1931).

interest on installation cost is more than enough to pay for chlorine at present prices. Since other operating costs are low, even if the recovered sludge be considered of no value, the process compares favorably from an economic standpoint with any other method that has been devised for the treatment of packing plant wastes.

The ultimate value and use for the sludge is problematic. On feeding the dry sludge to rats we found that it was toxic. Young rats died in four days when fed the dry sludge as the sole source of nitrogen. By extracting the sludge with ether or petroleum ether, the toxicity was reduced to a point where it was doubtful whether the effects produced were due to toxic materials or to the lack of certain essential amino acids. On feeding the extracted material to hogs along with corn no ill effects could be observed, and the animals showed a greater gain in weight than controls getting corn only. These preliminary results warrant further investigation, the results of which may show that the precipitated protein can be rendered fit for hog food. In case this cannot be done, it is felt that the sludge will have real value as nitrogen fertilizer. Experiments are now in progress to determine its value in this respect.

*Department of Bacteriology and Immunology,
 University of Minnesota.
**Geo. A. Hormel and Co.

THE STRUCTURE OF RUBBER AND OTHER ELASTIC COLLOIDS

BY G. S. WHITBY

Efforts have been made in recent years to ascertain the structure of rubber and explain its properties, by consideration particularly of (a) the structure of the globules in rubber latex, (b) the behaviour of rubber towards swelling agents (especially ether), (c) the X-ray diagram given by rubber under certain conditions. The purpose of the present paper is to consider current views concerning the structure of rubber, and also to point out that, since other colloids are known which exhibit in greater or less degree elastic properties similar to those exhibited by rubber, any general view of the structure of rubber can—it must be assumed, unless cogent reasons to the contrary are adduced—be regarded as acceptable only if it is also applicable to such other colloids. Its purpose is, further, to suggest that a study of such other elastic colloids is helpful in elucidating the structure of rubber.

A microscopical study (using the micromanipulator) of the globules in *Hevea* latex led Freundlich and Hauser[1] to conclude that the globules consist of rubber in two distinct forms: that they are composed of "a viscous liquid surrounded by an elastic shell".[2] The inner portion of the globule was considered as being caoutchouc in a lower and the outer as caoutchouc in a higher state of polymerization. The two forms of rubber hydrocarbon which these authors believed to be recognizable in the globules were at first assumed[3] to be identical with the parts, sol and gel, obtainable from raw rubber by the ether diffusion process (*vide infra*), but more recently Hauser has apparently modified this opinion.[4]

Von Weimarn[5] has concluded that the microscopical phenomena presented by rubber latex cannot be interpreted as proving the presence of a solid shell of rubber on the outside of the globules; and the present writer's observations, using the micromanipulator, are in agreement with this conclusion.

Leaving aside the question of the structure of the globules in rubber latex, a two-phase structure of a lower order, not recognizable by microscopic examination, has been considered to be present in rubber by many recent writers and has been made the basis of explanations of many of the properties of rubber. The two phases in question are usually known as sol and gel rubber and are distinguished by the fact that they are respectively soluble and insoluble in ether.

In point of fact the idea that raw rubber consists of two parts, identical in proximate composition, but one soluble and the other insoluble, is an old idea which has been lately revived and made the basis of explanations of some of the more striking modern phenomena observed with rubber, especially by means of X-rays. The idea was expressed by Payen,[6] Herbst,[7] Gladstone and Hibbert[8] and Weber.[9] Caspari,[10] by treating raw rubber with petrolic

ether, separated it into a soluble and an insoluble portion, the latter of which he referred to as the "pectous" form of rubber. He believed that it was possible to make a definite separation of rubber into the two forms, and that the proportions in which they occurred varied from sample to sample, and could be determined quantitatively. Stevens[11] reported, however, that, on repeating Caspari's experiments, he had been unable to obtain concordant results in repeat experiments. "The proportion of soluble to 'pectous' appeared to depend on the period of extraction." "Moreover," he said, "I find that the 'pectous fraction', if allowed to stand sufficiently long in cold petroleum spirit, dissolved wholly, with the exception of a small quantity of slimy nitrogenous matter which settled to the bottom of the containing vessel."

In recent years Caspari's views concerning the twofold nature of rubber have been revived; in the first place by Feuchter,[12] who applied ethyl ether instead of petrolic ether for the separation of the two parts. The portion of raw rubber which diffuses into ether when the rubber is allowed to stand in that liquid, and which corresponds to Caspari's "soluble" rubber, Feuchter designated Diffusion or D-rubber, while the portion which remains, and which corresponds to Caspari's "pectous" rubber, he designated as the gel skeleton. These two parts are now commonly known as sol and gel rubber, respectively, although Hauser[2] prefers the terms alpha- and beta-rubber. According to present usage, sol rubber is such portion of raw rubber as diffuses from the swollen mass into the solvent when rubber is allowed to stand in ethyl ether, whereas gel rubber is such portion as remains behind.

The view that rubber consists of two parts sharply separable by means of ether has been much in the foreground in recent years. Several writers,[13] among whom Hauser is prominent, have seen in the presence of sol and gel portions in rubber an explanation of the X-ray diffraction phenomena which rubber shows when stretched. It has also been called upon to explain the behaviour of rubber on mastication,[14] the Joule effect,[15] and the elastic behaviour of rubber generally; and, further, has been made the basis of an explanation of vulcanization.[16]

Although in its normal unstretched condition, raw rubber, when examined by X-rays, gives only an amorphous ring, it gives a fiber diagram with X-rays when strained beyond about 80 per cent.[17] If the amount of strain is gradually increased to say 1000 per cent, the interference spots on the X-ray diagram gradually increase in intensity but do not change in position. It has been supposed that the appearance of a diffraction pattern on stretching rubber is due to the occurrence of a "de-swelling" of the gel by the sol phase. Such a de-swelling seems to the present writer improbable. Assuming that the phases are to be regarded as imbibed each by the other, they are in the normal condition swollen to an extent far short of their maximum capacity for swelling, and it seems unlikely that mere extension would produce a syneresis. Elastic colloids (e.g. vulcanized rubber), after being caused to imbibe ten or more times their own weight of a liquid, can be stretched without any apparent occurrence of syneresis. And it does not seem likely that a syneresis on

stretching would occur in raw rubber, where, on the view under consideration, the higher polymeric phases are swollen only slightly and where the "swelling agent" is itself a solid, namely the lower polymeric phase.

If raw rubber is kept for a considerable time at a low temperature, until it becomes "frozen," it then gives with X-rays a Debye-Scherrer diagram in the unstrained condition. This has been attributed to an increase in the gel component at the expense of the sol component during the period of storage at a reduced temperature. Conversely, it has been supposed that on subjecting rubber to heat or mechanical working a change of gel to sol takes place, and that on keeping rubber which has been so treated the change gradually reverses itself, the rubber tending to regain its original properties.[18]

X-ray studies of stretched elastic colloids cannot yet be said to have solved the problem of the cause of elasticity in such materials. It is true that raw rubber, when stretched to moderate elongations, gives an X-ray diffraction pattern, which indicates that certain parts of the material have assumed a definite configuration, but vulcanized rubber, which has better elastic properties, requires to be stretched much further before it gives a pattern, while polyvinyl acetate shows no pattern at 1500 per cent elongation and polystyrene none at 1300 per cent elongation.[19] It would seem that the regular orientation of parts which an X-ray diffusion pattern connotes is not essential to the possession of elastic properties. Indeed, the occurrence of such a pattern is rather to be regarded as indicating that the material is assuming the character of an inelastic fiber.

The assumption of a fibrous character by rubber when it is stretched can be readily demonstrated, as Hock[20] showed, by cooling stretched rubber until it becomes brittle and shattering it by a blow. Other writers[21] have shown that when rubber is stretched and then cooled until almost inextensible, the tensile strength is higher the greater the original stretch. Thus Mark and Valko[22] found that a sample of raw rubber which had a tensile strength of 360 kg./cm.^{2} at 195°, had a tensile strength of 2470 kg./cm.^{2} if stretched 700% before cooling. This is in accord with the general property of fibers, first demonstrated by Herzog[23] for rayon, that the greater the degree of orientation of the elements of the fiber, the greater is the tensile strength.

Experimental evidence, some of which will be outlined in what follows, clearly shows that rubber and other elastic colloids are highly heterogeneous. Hence, in the opinion of the present writer, the view that rubber consists of two parts, "sol" and "gel," represents far too great an initial simplification of the issues involved in describing the nature of rubber and explaining its elastic behaviour. In the writer's view rubber does not consist of caoutchouc in merely two states of polymerization but is a mixture of an unbroken series of polymers representing a rather wide range of degrees of polymerization.

That the X-ray diffraction pattern given by stretched rubber is not due to the presence of two forms of rubber, one diffusible into swelling agents and the other not thus diffusible, is shown by the fact that diffusion-caoutchouc itself gives a pattern. A sample of diffusion-caoutchouc, prepared by removing the resin from raw rubber by cold extraction with a petrolic ether-

acetone mixture (3:7) and then allowing the rubber to stand in benzene until a portion of it had diffused into the solvent, was examined at extensions of 300% and 1800% . At both it gave a diffraction diagram, the diagram at the latter extension being remarkably sharp.[24]

In other respects too, diffusion-caoutchouc shows all the normal behaviour of rubber. Naturally, its behaviour is not quantitatively identical with that of the original rubber from which it is obtained, since it represents only a fraction of the latter and the range of polymeric states in it is not identical with that in the original rubber. It can, however, be vulcanized, especially if small proportions of fatty acids are added to replace those removed in freeing the rubber from "resin" before diffusion; it shows "racking" phenomena (cf. infra); it requires breaking down on a mill in making up a stock, and the ease of breakdown is not strikingly different from that of the original rubber. The last-mentioned observation is opposed to the attempts which have been made to describe the phenomena involved in the mastication of rubber on the basis of its supposed dual nature. The fact that rubber must be "broken down" by mastication on a hot mill in order to render it plastic has been ascribed to the necessity of rupturing the shells supposed to surround the liquid centres of the latex globules or more generally to producing a dispersion of the gel rubber in a continuous medium of sol rubber.

If the diffusion of a portion of raw rubber into a solvent is allowed to proceed only a short way, the diffusion-caoutchouc isolated is still an elastic solid substantially similar in physical consistency to the original rubber. If there were a liquid phase in rubber, it would be expected that this would appear first on extraction. The fractional extraction of rubber affords, however, no indication of the presence of a liquid phase.

A study of the behaviour of rubber towards solvents[25] clearly indicates that the degree of heterogeneity of rubber is much greater than that suggested by the sol-gel conception. The latter conception, as already stated, came to the fore as a result of Feuchter's separation in 1925 of rubber into a portion soluble and a portion insoluble in ether. Experiments started by the writer in 1923 on the behaviour of rubber in some 400 organic liquids show that rubber cannot be separated sharply into a soluble and an insoluble part, but that the portion which passes into solution depends greatly on the nature of the liquid employed, the length of time over which the solution or diffusion process is allowed to proceed, and other circumstances. It was early observed that when weighed pieces of raw rubber are placed in organic liquids, and the imbibition followed by weighing the pieces at intervals, in a large number of cases the weight at first rises and the later falls. That the fall is due to diffusion of part of the rubber from the swollen mass into the liquid can easily be shown by adding alcohol or other precipitant to the latter, when the diffused rubber is thrown out. The process of diffusion of rubber from the swollen gel goes on gradually over a long period and does not apparently ever come to a sharp end. Some of the samples were kept under observation for four years, and in many such cases the whole of the rubber with the exception of the protein ultimately became dispersed in the liquid. Even in relatively poor swelling

agents (see, e.g., o-tolualdehyde, octylene, isoamyl oxalate, chloracetal, cyclohexanone in Table I), the dispersion process was often observed to have completed itself after 3-4 years. The general impression made by the mass of data which has been secured on the swelling of raw rubber is that in general the process of diffusion never comes to a definite end or allows of a sharp separation of the rubber into a "sol" and a "gel" portion. A little of the data is quoted in Table I.

<div align="center">TABLE I</div>

<div align="center">Imbibition of Organic Liquids by Smoked Sheet (Original Weight: 1)</div>

Liquid	1	2	3	7	31	62	4 years
			Weight after periods of days				
Octylene	6.68	4.46	4.22	3.31	—	—	Completely dispersed.
o-Tolualdehyde	3.67	4.66	4.88	4.00	1.65	—	,,
Chloracetal	5.99	5.57	4.71	2.50	1.18	—	,,
Cyclohexanone	6.14	4.84	2.83	1.40	—	—	,,
n-Valeric anhydride	1.84	2.44	2.95	3.39	—	—	,,
Isoamyl oxalate	1.51	2.13	2.76	3.40	—	—	,,
Ethyl-m-toluate	7.98	8.39	8.25	6.07	2.92	2.36	
Isobutyl acetate	9.00	8.90	6.96	3.10	1.61	—	
p-Tolualdehyde	2.83	3.59	4.15	4.24	2.41	0.87	
o-Tolunitrile	5.67	7.10	7.79	7.43	4.82	2.43	
n-Propyl ether	5.98	5.25	4.29	3.03	2.27	1.87	
Safrole	9.51	11.60	12.01	10.36	5.86	4.51	
p-Cresyl ethyl ether	13.18	14.85	13.16	9.02	5.66	4.81	
Butyrophenone	4.83	5.95	6.18	4.30	—	1.60	
Allyl isothiocyanate	7.44	9.60	9.65	5.63	2.82	—	
Lauryl chloride	7.49	8.52	7.86	5.76	3.02	—	
Phenyl ethyl bromide	7.23	9.03	9.26	5.36	2.91	—	
Nonylic acid	3.37	5.00	6.50	6.91	1.58	—	
Tripropylamine	9.50	7.02	5.45	4.09	2.85	2.12	

The examples quoted in Table I have been chosen to represent liquids belonging to a considerable number of different chemical types. The figures show the weight of the swollen mass after various periods of time, the initial weight being taken as 1. In some but not all cases the samples were examined after a lapse of four years. Most of the liquids are not among the most powerful swelling agents. With such powerful swelling agents the swollen mass is usually too weak to handle for the purpose of weighing after one day. It may be mentioned for purposes of comparison that the weight of e.g. benzene imbibed in one day by the specimen of rubber in question was 24.22 parts; of ether, 11.10 parts.

If the point at which the process of diffusion becomes very slow were to be taken as the end point, the proportions of "sol" and "gel" which it would be concluded that the rubber contained would undoubtedly vary greatly with the solvent used.

Although there is no sharp end to the diffusion process, the ease with which diffusion occurs and the proportion which will diffuse into the solvent with reasonable rapidity, vary in different liquids, and are apparently influenced by (a) the swelling power of the liquid, (b) its viscosity. Even in a given liquid the proportion of caoutchouc which will diffuse in a reasonable time from a given sample of rubber can be greatly modified. Such modification can be brought about by (among various means) adding small quantities of certain agents, especially strong organic bases and acids, which increase the amount of the liquid imbibed by the rubber. When studying the electro-viscous effect in rubber sols in 1924, the author employed diffusion into ether and petrolic ether for the purpose of securing acoutchouc free from protein and observed that the addition of small amounts of piperidine, diethylamine, sodium ethoxide and ammonia greatly increased the proportion of diffused caoutchouc obtained from a given sample of raw rubber. Previously it had been found that small amounts of piperidine increase the swelling of vulcanised rubber in benzene.[26]

The influence of bases on the swelling and dispersion of raw rubber may be illustrated by the following data:—

Smoked Sheet in Petrolic Ether (B.P. 25-45°).

	A	
	Pet. ether alone	Pet. ether containing 5 drops piperidine per 10 ccs.
Weight originally	0.1317 grms.	0.1075
Weight after swelling 24 hours	1.0925 grms.	1.7435 grms.
Increase in weight	735 per cent	1520 per cent

	B	
	50 ccs. pet. ether	40 ccs. pet. ether + 10 ccs. ethereal solution NH$_3$
Weight originally	0.60 grms.	0.60 grms.
Weight of diffused caoutchouc pptable after 8 days' standing	0.05 grms.	0.31 grms.

In a good swelling agent such as benzene the proportion of caoutchouc which will readily diffuse from a sample of smoked sheet is greater than in a poorer swelling agent such as ether or especially petrolic ether. Thus, for example, in an experiment in which 3.83 grms. smoked sheet was left in 190 ccs. benzene with occasional very gentle agitation, 75.5 per cent of the rubber has dispersed in 7 days.

A study of the behaviour of vulcanized rubber in swelling agents also fails to afford any evidence of the presence of two sharply distinct parts. In current writings on the structure of rubber less attention has been given to vulcanized than to raw rubber, although the elastic properties which any

theory of the structure of rubber must ultimately endeavour to explain are exhibited in much greater perfection by the vulcanized than by raw material. It, however, the X-ray diffraction phenomena shown by raw rubber are ascribed, as they currently are, to its two-fold (sol-gel) nature, then it is natural to assume that, since vulcanized rubber shows similar X-ray phenomena, it too consists of two parts, although the proportion in which the two parts occur may be regarded as different, owing to the conversion during vulcanization of a portion of the sol into the gel form. (Cf. Hauser: Trans. Inst. Rubber Ind., 1926, p. 243 :—"During vulcanization the liquid rubber phase is more or less gelled or polymerised.")

Observations on the behaviour of vulcanized rubber in swelling media show, as in the case of raw rubber, no evidence of the presence of two clearly distinct parts. It is usually said that vulcanized, in contradistinction to raw rubber, is insoluble in all liquids. The writer has, however, found that, by leaving fully-vulcanized rubber in swelling agents for periods up to four years in the dark, the rubber gradually dispersed in many cases, Further, the rubber dispersed completely or substantially so, and there was no indication of the presence of a soluble and an insoluble phase. Examples of liquids in which vulcanized rubber was observed to disperse completely in the course of time are ethyl benzoate, butyl acetate, butyl oxalate, ethylene glycol dipropionate and twenty-one other esters; methyl iodide, bromoform, isobutyl chloride, o-chlorotoluene and twelve other halogenated hydrocarbons; benzene, valeric acid, ethyl propyl ketone, cyclohexanone, butyl isothiocyanate, hexyl alcohol, and o-tolualdehyde, diisolbutylamine, n-propyl ether.*

A number of artificial colloids which show elastic and colloid properties fundamentally similar to those of raw rubber can readily be shown to be highly heterogeneous. Such materials, although less important industrially than rubber, are more tractable than rubber and a study of them is capable of throwing light on the structure and behaviour of rubber, not only in regard to the question of heterogeneity but also in other respects.

Examples of artificial elastic organic colloids are synthetic caoutchoucs from conjugated dienes of low molecular weight, reaction-products from fatty oils and sulphur, polymers of methyl acrylate and similar esters, polymers of styrene, vinyl acetate and ethyl itaconate, caoutchouc hydrochloride, the reaction product from isoprene and sulphur dioxide. The first three of these examples are elastic at room temperature; the others, when warmed or swollen. Of these materials polystyrene and poly-vinyl acetate have been most closely investigated.

Polystyrene at ordinary temperatures is a hard solid; clear, when in massive pieces or fibers; white, when precipitated. At ordinary temperature it is not elastic, the films being brittle and the powder friable, but, as was first observed by the writer,[27] when warmed or swollen, it shows elastic properties. The

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* In this connection it may be mentioned that the viscosity of such sols of vulcanized rubber is very much less than that of sols of raw of the same concentration in the same liquids. The former sols are now being studied more fully. It may also be mentioned that crystals obtained from some of the sols apparently represent vulcanized rubber in a crystalline condition. They are being made the subject of closer investigation.

elastic properties are essentially similar in kind to those of raw rubber. The following observations made by Whitby and McNally[28] will serve to indicate the nature of the elastic phenomena displayed by autopolymerized styrene and to show their general similarity to those of raw rubber.

(a) Both polystyrene and rubber have an "elasticity temperature" below which the material becomes inextensible or "frozen." For rubber, however, this temperature is somewhat below ordinary room temperature.

(b) Polystyrene shows the effect known in rubber as "racking"; that is to say, if stretched while above its elasticity temperature and then, while extended, cooled below that temperature, it retains the extension, and, if then heated above its elasticity temperature, retracts. (This phenomenon can readily be observed in raw rubber by stretching a strip of smoked sheet and then, while maintaining the extension, cooling it in a stream of cold water. The rubber will be found to retain its extension if now released, but when warmed slightly, as, for instance, by holding it in the palm of the hand, will undergo retraction. It should be mentioned that the term "racking" is not very clearly defined and has sometimes been used to denote particularly the extension of rubber at elevated temperatures to lengths greatly exceeding those to which it can be extended without rupture at ordinary temperature. In this usage of the term too, polystyrene can be "racked," i.e. at temperatures well above the elasticity temperature it can be extended to lengths much beyond those at which near the elasticity temperature it suffers rupture.)

(c) Like rubber, polystyrene shows elastic after-effect, i.e. on releasing a specimen which has been stretched, a slow retraction follows on the initial rapid retraction. This is shown by the following experiment. A strip 6 cms. long was placed in water at 95°, stretched to a length of 22.5 cms., and then released under no-load. Table II gives the length of the strip at intervals after its release.

TABLE II

Retraction of Polystyrene

Time after release (secs.)	0	1	7	102	310	900
Length (cms.)	22.5	10	9	8	7.5	7

(d) When the material is stretched and then released, the amount of set left after any time is profoundly influenced by the length of time for which the material has been maintained in a stretched condition. In an experiment, strips of polystyrene were stretched 450 per cent at 95°, and, after being held at this extension for various periods of time, were released. The retraction over a period of time was followed. The data in Table III indicate the character of the results obtained.

TABLE III

Influence of Period of Stretching on Retraction of Polystyrene

Time kept at 450% (mins.)	0	5	10	90
Extension immediately after release (%)	50	150	175	300
Extension 200 secs. after release (%)	0	55	75	150

The following experiment carried out with strips of raw rubber (smoked sheet) shows that the set in rubber is similarly influenced by the length of the period of time for which the material is maintained in a stretched condition. Strips were held at an elongation of 200 per cent at 48° for various periods of time, and, after being released, they were allowed to stand at room temperature for ten days, when no further retraction could be observed. The set remaining is tabulated as E_1. The strips were then heated for one hour at 100°, and, after they had been allowed to cool to room temperature, the set (E_2) was again measured. The results are given in Table IV.

TABLE IV

Set in Raw Rubber after Extension for Various Times

Time kept at 200% at 48° (mins.)	Set at room temperature (%) E_1	Set at 100° (%) E_2
5	22.5	17.5
10	27.5	17.5
15	37.5	20
30	40	27.5
60	52.5	35
120	62.5	42.5
240	67.5	47.5

(e) The higher the temperature at which either rubber or polystyrene is stretched to a given extent, the greater is the set remaining on release. This was observed qualitatively for polystyrene. For raw rubber more exact data were secured. Strips of smoked sheet were held at different temperatures for 30 minutes at an extension of 200 per cent, and were then allowed to retract at room temperature for 10 days (set: E_1) and subsequently were heated to 100° and the set (E_2) again measured. Table V gives the results.

TABLE V

Influence of Temperature of Stretching on Set in Raw Rubber

Temperature during extension	Set at room temperature (%) E_1	Set at 100° (%) E_2
20°	17.5	15
25	22.5	15
35	30	20
40	47.5	22.5
60	55	45
70	70	55
83	90	75

(f) Both with polystyrene and with rubber, the greater the length to which a specimen is extended, the greater is the set present under given conditions. This was determined only qualitatively for polystyrene. For rubber (smoked sheet) the following more exact data were secured.

TABLE VI

Effect of Original Elongation on Set in Raw Rubber

Elongation maintained for 30 minutes at 48° (%)	Set after 10 days at room temperature (%) E_1	Set at 100° (%) E_2
50	7.5	7.5
100	20	17.5
150	27.5	20
200	40	27.5
250	55	30
350	125	52.5
400	142.5	—

(g) The following experiment was carried out on a strip of polystyrene of cross section 2.05 sq. mm. A constant load of 75 grms. was maintained throughout; the temperature was first raised at a definite rate; then lowered; again raised, and so on. The elongation at the end of each period of heating and cooling and at certain intermediate points is shown in the following Table.

TABLE VII

Heating and Cooling Polystyrene under Fixed Load

Temperature Rising	Falling	Elongation (%)	
1. 55°		0	
65		10.8	
75		35.2	
80		457	
	1 a. 70°		473
	64		481
	40		481
2. 67		481	
70		495	
79		523	
	2 a. 74		528
	70		528
3. 79		560	
	3 a. 25		560
4. 79		590	

These results indicate a behavior analogous to that of rubber in two respects. (a) During the first period of cooling, it will be noticed, "creep" takes place until the temperature has fallen below the elasticity temperature. (b) During the periods, 1, 2, 3, 4, the final extension increases in each succeeding period, but the difference between the extension at the end of the first and of the second period is greater than the difference between that at the end of any other two successive periods. This clearly recalls the behavior of rubber when sub-

jected to successive cycles of extension and retraction. With rubber, the difference between the first and the second cycles is greater than that between any other two successive cycles (see Whitby, Plantation Rubber and the Testing of Rubber, 1920, Chap. XVIII).

(h) It has been shown by Rosbaud and Schmid (Z. tech. Physik, **9**, 28 (1928)) that even extremely small loads will cause raw rubber to extend and will even rupture it if allowed to act for sufficiently long periods. A similar behaviour was observed with polystyrene. For example, while a load of 45 grms. applied at 95° to a strip 2.13 sq. mm. in cross section caused relatively rapid stretching and produced an elongation of 122 per cent in 5 seconds, even a load of 5 grms. would produce the same elongation if allowed to act for 225 seconds.

(i) Sols of autopolymerised styrene show many similarities to sols of rubber. At the same temperature and in the same solvent sols of rubber and of polystyrene have similar viscosities. The nature of the solvent affects the viscosity of sols of the two materials in, broadly, a similar way. The lowest viscosities in both cases were observed in the same solvent, viz. acetal.

Poly-vinyl acetate has also been shown to possess elastic properties similar to those of polystyrene.[29]

The high degree of heterogeneity which has been shown to be characteristic of high polymers in general[30] has also been found to exist in elastic polymers. Data showing the heterogeneity of poly-vinyl acetate have already been put on record.[29] The following data show that polystyrene is heterogeneous. A sample of polymer prepared by heating styrene for four days at 245° was separated by fractional precipitation with alcohol from solution in benzene into six fractions. The fractions had molecular weights as follows:[31]

TABLE VIII

Fractionation of Thermo-Polymerized Styrene

Fraction No.	1	2	3	4	5	6
Mol. wt.	4405	2914	2632	1979	1274	977

The heterogeneity of autopolymerized styrene was demonstrated by determining the viscosity of sols prepared from fractions secured by means of fractional precipitation and by means of fractional solution.

A sample of synthetic methyl caoutchouc, prepared by the thermo-polymerization of 2:3-dimethylbutadiene-1:3, was found to be resolvable into fractions having different properties, as the following data will show:

TABLE IX

Fractionation of Methyl Caoutchouc

Fraction No.	1	2	3
Time of flow of sol (0.854 gm. in 20 ccs. benzene) (secs.)	55.4	67.8	81.3

Direct experimental evidence has also been secured of the fact that natural rubber shows a degree of heterogeneity similar to that of the artificial elastic colloids mentioned above. The diffusion of swollen rubber into the swelling agent was carried out fractionally, fractions being poured off and fresh liquid added from time to time. The sols thus obtained were found, after being adjusted to the same caoutchouc content, to differ widely in viscosity. Diffused rubber was also separated by fractional precipitation into fractions having different properties. The data obtained in this connection will be published elsewhere. They afford conclusive evidence that raw rubber considered as a whole and also diffusion-caoutchouc ("sol" rubber) are far from homogeneous.

In the case of solid polymers obtained from styrene by means of heat, heterogeneity is easily recognizable when the materials are treated with ether, acetone or ethyl oxalate. When the much more highly polymerized product obtained by allowing styrene to undergo autopolymerization is treated with ether or acetone, no solution or apparent swelling takes place, and when treated with diethyl oxalate, only a very slight swelling. When, however, styrene polymerized by heating at 140° or 180° is treated with these liquids, the major part rapidly goes into solution, but there remains a portion which fails to disperse and which on standing settles out as a white powder. This is clearly a fraction of the material more high polymerized than the rest. If it is separated and treated with benzene (a solvent for highly-polymerized styrene), it readily goes into solution.[28]

The ease of dispersion of colloidal polymers derived from a given monomer depends on the degree of polymerization. Thus the product obtained by the spontaneous polymerization of styrene disperses far less than the much less highly polymerized product obtained by heating styrene. The fact that rubber, like other elastic colloids, consists of a mixture of polymers covering a rather wide range of molecular sizes is in full accord with observations outlined earlier on its behaviour to a variety of swelling agents. In a homologous series of polymers the extent to which swelling agents are imbibed rises and the ease with which dispersion takes place falls, as the series is ascended. Futher, imbibition by and dispersion of a given polymer is different in different liquids. Hence, the proportion of a given sample of raw rubber which will pass readily into the solvent, *i.e.* the proportion of "sol" rubber obtained, differs in different liquids.

As the higher polymers disperse more slowly than the lower, the rate at which a sample of rubber disperses falls as the proportion which has undergone dispersion increases. Even the highest polymers present will, however, if given time, disperse in many solvents, and hence, as already stated, the whole of the rubber disperses in many cases if left to stand for a long time. The protein network present in rubber may possibly retard the dispersion of the caoutchouc somewhat, but can hardly be regarded as the main cause of the slowness with which the higher fractions of rubber disperse. In this connection it may be noted that diffused rubber (obtained by means of petrolic ether), although free from protein, was found after being vulcanized to behave in solvents essentially similarly to ordinary vulcanized rubber. Vulcanized

fatty oils, in which too a protein network is lacking, were observed to disperse more and more slowly, as the period of vulcanization and, as it may be assumed, the degree of polymerization, increased. After the polymerization of a sulphurized oil (containing no free sulphur) had proceeded just to the point at which the material had set solid, the product dispersed readily in benzene, but, as the polymerization was carried further by continued heating, dispersion became slower and slower, and finally a product was obtained, which, like vulcanized rubber, dispersed in benzene only after standing for several years.

A striking case of the difficulty of dispersion due apparently to a high degree of polymerization is presented by poly-methyl acrylate. This material, which was prepared by heating methyl acrylate for half an hour on the water-bath with o.1 per cent benzoyl peroxide, has a molecular weight so high that it produces no appreciable depression of the freezing point of benzene. It shows greater swelling than any other polymeric product which has been examined by the writer, taking up, e.g., 88.8 times it weight of methyl acetate; yet it failed to disperse in any reasonable time even in good swelling agents.

Not only the ease of dispersion in solvents, but many other properties of organic colloids are influenced by the degree of polymerization. This has been shown to hold for the melting point of a series of polymers such as the poly-indenes;[32] for the softening point of elastic colloids such as fractions of poly-styrene and poly-vinyl acetate; for the ease of cracking on pyrolytic decomposition in the case of polyindenes[33] and polystyrenes, and for the viscosity of sols of a given concentration.[29] It also holds for the elastic properties, as may be well illustrated by reference to polystyrene.

As obtained by allowing styrene to undergo spontaneous polymerization at room temperature, polystyrene has a molecular weight of the order of 100,000 or more; it produces an almost inappreciable depression of the freezing point of benzene. The data quoted earlier in regard to the physical properties of polystyrene all refer to such material. As obtained by heating styrene, however, polystyrene has a lower and measurable molecular weight and correspondingly possesses a lower elasticity temperature and poorer elastic properties. A sample prepared by heating styrene for 48 hours under reflux at 140° had a molecular weight, determined cryoscopically, of 1920; and one prepared by heating styrene for 24 hours in a closed vessel at 180°, a molecular weight of 2180. These samples became soft at 40° and readily extensible at 47°, whereas the corresponding figures for autopolymerized styrene were 65° and 75°. While they could be extended readily, their power of retracting was poor and they showed a vast amount of set when the extending stress was removed. At 72° a specimen stretched 800 per cent and then released, re-tracted to 600 per cent and remained there. A specimen extended to 1400 per cent at 89° and then released, retracted only to 1100 per cent and re-mained there.[28] Compare the data for autopolymerized styrene in Tables II and III. Synthetic rubber also illustrates the influence of the degree of poly-merization on the elastic properties. A sample of synthetic rubber made by heating isoprene at 85°, found to have a molecular weight of about 4000—far lower than that of natural rubber—and to give sols of much lower viscosity

than those from natural rubber, had, correspondingly, elastic properties much inferior to those of raw rubber.

Since the properties of elastic polymers derivable from a given monomer are clearly dependent on the degree of polymerization, the properties of a given sample of materials such as those under discussion in the present paper will be determined both by the mean molecular weight of the material and the range of molecular sizes in the mixture of which the material is composed. For the polymeric products obtainable from a given monomer there is probably a certain degree of polymerization which is optimal for the possession of good elastic properties. If the degree of polymerization is too low, the material, while readily deformable, shows poor recovery from deformation, *i.e.*, it shows a large amount of set when allowed to retract after deformation; if the degree of polymerization is too high, the deformability is small and the material is tough, or, in the highest states of polymerization, brittle or "short." In a certain intermediate state of polymerization, the material is both deformable and retractable.

A consideration of data such as those given to illustrate the elastic behaviour of polystyrene and raw rubber shows that the materials are not perfectly elastic; that on allowing them to recover after deformation, recovery is not immediate and complete, but that there is a certain amount of set. The amount of set is dependent not only on the degree of polymerization, but is also greatly influenced by other factors. The longer the period of time for which the material is kept stretched the higher the temperature at which it is stretched and the greater the extent to which it is stretched, the greater is the set.

Further there are three kinds of set, viz. (a) that which disappears in time at ordinary temperature, (b) that which remains permanently at ordinary temperature but disappears on raising the temperature ($E_1 - E_2$), (c) that which remains permanently even on raising the temperature (E_2). Set of the first and of the last types, *i.e.* sub-permanent and permanent set, are due chiefly to the lower polymers present. Set of the second kind, which is permanent at ordinary temperature, but sub-permanent at an elevated temperature, may for convenience be referred to as apparent set and is of special interest. It is due to the fact that, although retractive forces are still present in the material, they become apparent only when the internal viscosity of the material is reduced by increasing the temperature.

What has just been referred to as the viscosity might perhaps more correctly be termed the "elastic yield value." The potential retractive forces in the material are unable to effect refraction because the yield value is too high, unless the temperature is raised. As the unqualified term "yield value" has been assigned to the deformation and flow of plastic materials, it would seem desirable in the case of elastic materials to refer to "elastic" yield value. This yield value is significant in connection with other phenomena presented by elastic colloids as well as in connection with apparent set under that aspect of it just discussed. If a strip of polystyrene is stretched and then, while stretched, cooled below its elasticity temperature, it sets hard and retains its

extension indefinitely at room temperature. The material now presents an extreme case of apparent set. If it is warmed to above its elasticity temperature (the temperature at which the elastic yield value is less than the ultimate breaking stress), the elastic yield value becomes reduced sufficiently to permit the potential retractive forces to become effective, and consequently the material retracts. Polystyrene can also be rendered deformable at ordinary temperature if the elastic yield value is reduced by causing it to imbibe a swelling agent. Another phenomenon which is probably due to reduction in the elastic yield value as a result of increase of temperature is the retraction which follows the application of warmth to a strip of rubber under load. This phenomenon is one aspect of what is known as the Joule Effect.[34] Similarly the removal of "grain" from milled rubber by means of a hot table depends on the reduction of the elastic yield value. The same effect, viz. the release of internal strains in calendared rubber sheet, may be brought about, as Weigand showed,[35] by applying a swelling agent.

The effect of swelling agents in reducing the elastic yield value, and thus rendering elastic colloids which are not normally so, is not confined to the cases, such as polystyrene and poly-vinyl acetate, which have already been mentioned. It is also observable with hydrophilic colloids such as the proteins, silk fibroin and wool keratin. Von Weimarn[36] records that when silk fibroin is dissolved in certain concentrated aqueous salt solutions and then precipitated by the addition of alcohol, it shows elastic properties when the degree of hydration is suitable. "As the degree of dehydration increases," he says, "we may witness the realisation of every possible transition stage marking the gradual conversion from the condition of an extremely viscous syrup through a gluey mass to that of an elastic caoutchouc-like jelly (in which condition an *elastic* extension to twice or even four times the former length is possible) and thence to that of masses possessing the consistency of an animal tendon, till it finally reaches the state of an altogether solid mass, so solid that when in thin sheets it may be broken."

Similarly, the elastic properties of wool are greatly influenced by the extent to which the protein is swollen by moisture in the fibre.[37] If a wool fibre containing the normal water-content is stretched and then, while stretched, is dried, it will be found to retain its extension on release, but will then re-'tract if again allowed to absorb moisture, i.e. if the elastic yield value of the protein is reduced by allowing it to swell somewhat. Advantage is taken of this phenomenon in the treatment of wool known as "crabbing."

Although wool is much less extensible than rubber, there is broadly an analogy, not only in this respect, but also in other respects between the elastic behaviour of wool and of raw rubber. In both cases time plays an important part in the result of any series of mechanical manipulations through which the material may be made to pass. Strictly speaking, there is no such thing in either case as a stress-strain diagram, but only a stress-strain-time diagram. This is perhaps more obvious with wool than with rubber. On loading a wool fibre, there occurs first a rapid extension, which is reversible, and this is

followed by a further, slow extension, which is only partly reversible and is greatly influenced by the length of time over which the load acts, owing to plastic flow of material.

The ultimate explanation of the fact of elasticity in elastic organic colloids cannot yet be given with any sufficient degree of definiteness. It seems desirable to bear clearly in mind that what distinguishes elastic materials from other deformable materials, such as plastic solids or viscous liquids, is, not their ability to undergo deformation, but their power to recover from deformation. The important feature which calls for explanation is not their deformability but their retractability. It has recently been suggested that the explanation of the elasticity of rubber is to be found in the shape of the molecules themselves. The molecules are regarded as helical in shape. It is supposed that on stretching rubber the spirals straighten out and that "the force which causes the extended chains to coil again into spirals when the stress is released is the residual valencies of the double bonds."[38] On this view the retraction is due to the attraction of the double bonds in the caoutchouc molecule for each other. But the molecules of many other elastic colloids are saturated or substantially so. Polymers of styrene, vinyl acetate and methyl acrylate, for example, are capable of retracting after extension despite the absence of double bonds. In support of their view that the retractibility of rubber is due to its double bonds Fikenscher and Mark quote the fact that if the double bonds are saturated with hydrogen chloride the product is inelastic. It may, however, be pointed out that caoutchouc hydrochloride is only apparently inelastic, since, although inelastic at ordinary temperature, it shows elastic properties when warmed.[27]

Further, according to the view of Fikentscher and Mark, mere unfolding of the spiral molecules will permit of rubber being stretched sixfold. Only beyond that extension is the lattice actually stretched, and, they imply, will permanent set appear. The data given on pages 208-209 of the present paper show, however, that permanent set can be produced in rubber at much lower extensions than 600 per cent.

It may well be supposed that the forces which bring about the retraction of elastic colloids after deformation are essentially the same as those which produce cohesion in the unstrained material. Elastic solids stand between brittle solids on the one hand and liquids on the other in regard to the strength of the cohesional forces involved. In a brittle solid cohesion is such that, on applying stress, rupture takes place before change of shape. In a liquid, change of shape occurs with great readiness and the cohesional forces are insufficient to restore the shape. In an elastic solid, subjected to stresses below the breaking stress, the cohesional forces are insufficient to prevent change of shape but sufficient to restore the shape when the stress is removed.

In imperfectly elastic materials, such as are under discussion in the present paper, the phenomena are complicated by the fact that the materials are mixtures of polymers which differ in regard to the strength of the cohesional forces associated with them. It seems probable that the forces involved in the elastic behaviour of these materials are not only, and perhaps not chiefly,

the primary valencies or lattice forces, but secondary forces such as the force of association responsible for the abnormal viscosity of all but the most dilute sols of these colloids.

References

[1] Freundlich and Hauser: Kolloid-Z. Zsigmondy Festschrift, **36**, 15 (1925).

[2] Hauser: Trans. Inst. Rubber Ind., **1926**, 239.

[3] Freundlich and Hauser: Loc. cit.; cf. Hauser: Ind. Eng. Chem. **18**, 1146 (1926); Trans. Inst. Rubber Ind., **1926**, 239; Bary and Hauser: Rev. gén. Caoutchouc, **1928**, 3.

[4] Hauser: Ind. Eng. Chem., **21**, 249 (1929).

[5] Von Weimarn: Rep. Imp. Ind. Res. Inst., Osaka, **9**, No. 5, 1 (1929;) Bull. Chem. Japan, **3**, 157 (1928).

[6] Cf. Weber: J. Soc. Chem. Ind., **19**, 215 (1900).

[7] Herbst: Ladenburg's "Handwörterbuch der Chemie," **5**, 479 (1887).

[8] Gladstone and Hibbert: J. Soc. Chem. **53**, 679 (1888).

[9] Weber: Ref. 6.

[10] Caspari: J. Soc. Chem. Ind., **32**, 1041 (1913).

[11] Stevens: J. Soc. Chem. Ind., **38**, 194T (1919).

[12] Feuchter: Kolloidchem. Beihefte, **20**, 434 (1925).

[13] Hauser and Mark: Kolloidchem. Beihefte, **22**, 63; **23**, 64 (1926); Gummi-Ztg., **40**, 2090 (1926); Kautschuk, **1925**, 10; Hauser: Ind. Eng. Chem. **18**, 1146 (1926); **19**, 169, (1927); Trans. Inst. Rubber Ind., **1926**, 239; Ind. Eng. Chem., **21**, 249 (1929); Bary and Hauser; Rev. gén. Caoutchouc, **1928**, 3.

[14] Hauser: Kolloid-Z., Spec. No., April (1925); India-Rubber J., **69**, 663 (1925); Park: Ind. Eng. Chem. **17**, 160 (1925).

[15] Freundlich and Hauser: Kolloid-Z., Zsigmondy Festschrift, 15 (1925); Hauser and Mark: Kolloidchem. Beihefte, **23**, 64 (1926).

[16] Hauser: Trans. Inst. Rubber Ind., **1926**, 243.

[17] Katz and Bing: Z. angew. Chem., **38**, 439 (1925); Katz: Naturwissenschaften, **13**, 410 (1925).

[18] Bary and Hauser: Rev. gén. Caoutchouc, **1928**, 3.

[19] Whitby, McNally and Gallay: Colloid Symposium Monograph, **6**, 225 (1928).

[20] Hock: Z. Elektrochemie, **31**, 417 (1925).

[21] Rosbaud and Schmid: Z. techn. Phys. 9, 98 (1928); Hauser and Rosebaud; Kautschuk, **4**, 12 (1928). Cf. Le Blanc and Kröger: Kolloid-Z., **27**, 205 (1925).

[22] Mark and Valko: Rev. gén. Caoutchouc, **7**, 11 (1930).

[23] Herzog: Ber., **58**, 1254 (1925).

[24] Thanks are due to Dr. T. N. White for taking these diagrams.

[25] Shortly to be published in detail in Can. J. Research.

[26] Whitby and Jane: Colloid Symposium Monograph **2**, 16 (1924).

[27] Colloid Symposium Monograph, **4**, 243 (1926).

[28] Whitby and McNally. Full data will appear shortly in Can. J. Research.

[29] Whitby, McNally and Gallay: Trans. Roy. Soc. Canada, **22**, III, 27 (1928); Colloid Symposium Monograph, **6**, 225 (1928).

[30] Cf. e.g., data showing the heterogeneity of polyindene, poly cinnamal fluorene, poly cinnamal indene, polyisosafrole, polyiseugenol, Whitby and Katz: J. Am. Chem. Soc., **50**, 1160 (1928); Can. J. Research, **4**, 344, 487 (1931); Staudinger e.g. Helv. Chim. Acta **12**, 922 (1929).

[31] Whitby and Katz: Can. J. Research, forthcoming.

[32] Whitby and Katz: J. Am. Chem. Soc. **50**, 1160 (1928); Can. J. Research, **4**, 344 (1931).

[33] Whitby and Katz: Can. J. Research, **4**, 344 (1931).

[34] Cf. Whitby: "Plantation Rubber and the Testing of Rubber," Chap. XX (1920).

[35] Ref. 34, p. 484.

[36] Von Weimarn: Reps. Imp. Ind. Res. Inst., Osaka, **8**, No. 13 (1927).

[37] Cf. Shorter: J. Textile Inst., (1924); Trans. Faraday Soc., (1924); J. B. Speakman, **25**, (1929); **26**, 61 (1930).

[38] Fikentscher and Mark: Kautschuk, **6**, 2 (1930).

STUDIES IN CHRONAXIE*

BY WILDER D. BANCROFT AND G. HOLMES RICHTER**

The study of the phenomena of excitability in tissues has long been a favorite field of research for physiologists. The interest of chemists in this field is limited to the extent to which drugs will bring about alterations in the excitability and the interpretation of the phenomena, so far as possible, in terms of chemistry.

Fredericq[1] defines the excitability of a tissue as "the property it possesses of answering by a change in shape, state, or position to a modification occurring in the surrounding medium. That modification of the medium we call the stimulus. A stimulus may be either of a mechanical, thermal, luminous, or electrical nature. The stimulus evokes in the tissue an excitation, and this excitation, if transmitted to the active organ, becomes perceptible either by a muscular contraction, or a glandular secretion or by a change in the electrical state of the nerves, muscles, or glands. The real nature of the excitation, of the modification produced by the stimulus in the excitable tissue, we do not know. It may be imagined, according to the work of Nernst, to be an unequal distribution of ions at the boundaries of distinct colloidal phases: a hypothetical view that lacks, however, definite experimental confirmation."

The studies of these phenomena have been primarily of the relation of the stimulus to the modification produced in the tissue. The reason for this is that the stimuli, mentioned above, are purely physical agents and are consequently more readily investigated than the more complex biological phenomena. The stimulus usually employed is an electrical current, because of the ease in which it can be varied. In the early work in this field it was found that there was some minimum value of the stimulus below which no effect was produced. Various degrees of importance were attached to these minimum or threshold values.

Du Bois-Reymond[2] found that the electrical stimulus was effective only when the circuit was opened or closed; no visible change occurred during the passage of the current. If the intensity of the current was rapidly changed, the tissue would respond; but if the intensity was changed slowly there was no response. Du Bois-Reymond was unable to correlate any change in the threshold value with the time of application. That is, the threshold value was the same whether the stimulus was applied for one second or one hundredth second.

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[1] Physiol. Rev., **8**, 501 (1928).

[2] "Untersuchungen über thierische Electricität" (1848).

While such material may be quite interesting to physiologists there is little chemistry concerned, so we hasten on to the point at which the interest of chemists begin to crystallize. Lapicque[1] and others found that if the stimuli were applied for very short lengths of time there was a drift in the threshold values. He determined a relation between these quantities and defined arbitrarily a purely empirical value as characteristic of the excitability. This empirical value, the chronaxie, is easy to determine and allows one to compare the excitability of one tissue with that of another, which was entirely out of the question in the older method. Moreover, by means of this concept some very perplexing properties of drug action have become quite simple and clear.

FIG. I
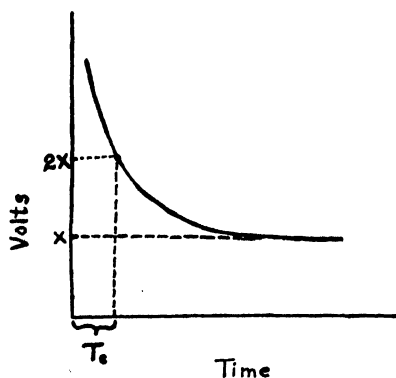
Let us define chronaxie. The relation between the time of application of the stimulus and the intensity of the stimulus is given graphically in Fig. 1. When the time of duration of the stimulus is very long the minimum effective voltage is x, this value is called the rheobase. If the rheobase is doubled, that is x changed to 2 x, and the shortest time determined at which stimulation will occur it will be found to be T_c, shown on the time axis, this value is called the chronaxie.

The actual chronaxie values vary over wide ranges for different tissues but are constant for any one normal tissue. Thus the chronaxie of the gastrocnemius muscle of the frog is 0.0003 second while the chronaxie of the muscles of the frog's stomach, which are less excitable, is 0.10 second. The investigations of Lapicque have brought about a better understanding of the conduction of the nerve impulse from a nerve to a muscle. He was able to show that the chronaxie of a nerve and the muscle to which it was connected were the same. This condition is known as the law of isochronism. Certain drugs can alter the chronaxie of the muscle or nerve and when the values differ by a ratio of about two to one the stimulus is no longer effective; naturally such a condition would results in paralysis. The condition in which the two chronaxies are different is sometimes referred to as heterochronism.

The application of this concept to the action of several drugs can be best studied by starting with curare. If a nerve-muscle preparation is treated with curare and the chronaxies of the nerve and muscle are measured separately it will be found that the value for the nerve is unchanged while that of the muscle is increasing progressively. As soon as the value for the muscle becomes about twice as great as that of the nerve the impulses through the nerve are no longer able to stimulate the muscle and paralysis results. Paralysis would also occur if the chronaxie of the muscle had remained con-

[1] "L'Excitabilité en Fonction du Temps" (1926).

stant while that of the nerve became altered more than the two to one ratio. Thus there are four kinds of curarization, which are outlined in the table below. All of these except the second case have been studied.

TABLE I

Chronaxie of nerve	Chronaxie of muscle	Drug
(1) normal	increased	curare, spartein
(2) increased	normal	?
(3) decreased	normal	strychnine
(4) normal	decreased	veratrine

This theory also suggests a method of counteracting certain cases of this type of paralysis. Thus if strychnine is used alone it behaves as a curarizing drug, veratrine also has this effect. However, if both drugs are applied at the same time the stimulation of the muscle through the nerve is again possible. The reason for this is easy to see, strychnine decreases the nerve chronaxie until it is below the two to one ratio and paralysis results; veratrine, on the other hand, decreases the muscle chronaxie until it is below the two to one ratio so that if both drugs are acting simultaneously the two new values of the chronaxies, while below normal, are equal which is the necessary condition for the transmission of the nerve impulse to the muscle.

This simple and accurate explanation of the effect of these drugs is in striking contrast with the classical explanation. The older view was that the irritability of the nerve and muscle remained unaltered and the curarizing drug attacked some intermediate neuro-muscular substance which caused the paralysis. Needless to say, the evidence for these mysterious intermediate substances was never formidable.

There are many other interesting applications of the concept of chronaxie to problems in the field of biology and medicine. These application are however outside the scope of this paper, for we are interested in the effect of drugs on the chronaxie of nervous tissue and the variations it undergoes. Before discussing the experiments a brief description of the apparatus and method of measuring the chronaxie will be given.

In the first portion of this paper it was pointed out that the pioneer electro-physiologists erred in assuming that there was no relation between the intensity of the stimulus and the time of its duration. This error arose through the fact that for the frog's nerve-muscle preparation, which was mostly used, time intervals of 0.0003 seconds would be necessary before any marked change in the results would occur. Methods for producing and measuring accurately such short intervals of time were not readily available to the early workers. Even at a later date ballistic methods were used; that is two wires placed at various distances were cut by shooting a bullet through them, the time element was varied by changing the distance between the wires. This method was very inconvenient.

The method now in use depends upon the fact that the time of discharge of a condenser is a function of its capacity and the resistance in the circuit.

Thus, when a variable condenser is charged up to a given potential and then discharged through the preparation of constant resistance the duration of the electrical stimulus is a function of the capacity of the condenser. Such an arrangement is very convenient and requires no unusual form of apparatus.

The diagram of the hook-up is shown in Fig. 2.*
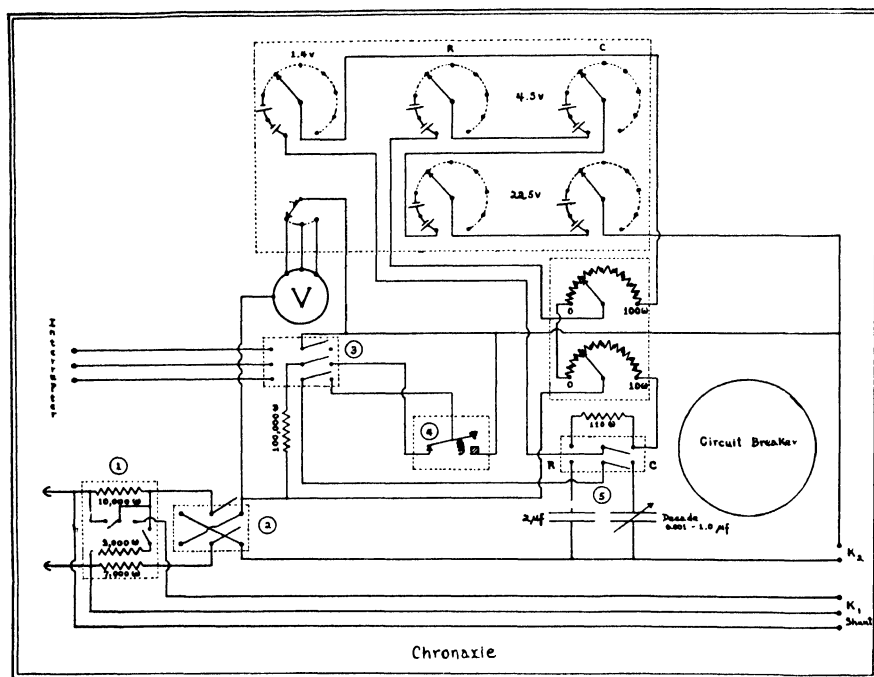
FIG. 2

A source of potential is provided for by ordinary dry cells and radio "B" and "C" batteries; these are arranged behind the panel shown in the upper part of the diagram. In making a determination of the chronaxie two silver wires coated with silver chloride are placed in the physiological salt solution that bathes the preparation; in the experiments in this laboratory this was always the nerve of the muscle-nerve preparation from the frog. These electrodes are connected with the resistance bank (1) and 10,000 ohms resistance placed across them. The switch marked (2) is merely a reversing switch, switch (3) is closed so that the key (4) is in the circuit and switch (5) is thrown to the left side marked "R," for rheobase. The apparatus is now ready for the determination of the rheobase, for the intensity of the stimulus can be varied by altering the voltage, and the time of duration of the applied stimulus will

be long because the two micro-farad condenser is the condenser that discharges through the nerve when the key (4) is tapped. The actual determination is accomplished by setting all the switches on the panel at zero and then increasing the potential by turning the smaller value switches up first, each time testing the nerve by tapping the key. When the potential is great enough the muscle contracts. Smaller gradations of the potential can be obtained by altering the resistance of the variable resistance above switch (5). The smallest potential that will cause the first visible twitch of the muscle is the desired rheobase. The actual value can be read off on the voltmeter on the panel.

The determination of the chronaxie, the time required to stimulate the preparation with a stimulus of twice the rheobase, is next carried out. The switch (5) is now thrown on the right hand side marked "C," for chronaxie, this places the variable condenser in circuit. The switches marked "C" on the panel are then altered such that the new potential is just twice that of the rheobase. This new potential of twice the rheobase is now flowing through the preparation and charging the variable condenser. By varying the capacity and testing each time, by tapping the key and discharging the condenser through the nerve, the smallest capacity is sought which will cause the first visible twitch of the muscle. When this is found, the chronaxie is given by the following expression:

$$\text{chronaxie} = \text{capacity} \times \text{resistance} \times 0.37$$

Lapicque evaluated the constant of 0.37 by calibrating against some more accurate method. The need for this constant arises through the characteristic discharge curve of condensers. Bouman[1] and Monnier[2] have calculated from theoretical considerations the value of this constant and found it to be 3/8 or 0.375.

Since the resistance is constant, the chronaxie is proportional to capacity and in this study of the variations of the chronaxie the values are given in terms of the capacity directly.

In our study of the coagulation theory of narcosis we were led to the interesting conclusion that there was a very close relation between narcotics and stimulants.[3] In low concentrations narcotics behave as stimulants and in high concentrations stimulants behave as narcotics. We believe that both stimulants and narcotics are coagulating agents for the proteins of the nervous system that is involved. After writing our paper, it was pointed out that this state of affairs could be easily investigated by a study of the variations of the chronaxie of the nervous tissue. A rather hasty survey of the field showed that in the majority of the cases the effect of a drug on the chronaxie of a tissue was reported as either an increase or in other cases as a decrease. According to our views, the chronaxie should first decrease, then return to a pseudo-normal state and later go above normal when the proteins of the system

[1] Arch. neérl. Physiol., **12**, 416 (1928).
[2] Soc. Biol. de Paris, **98**, 290 (1928).
[3] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

undergo a sufficient decrease in dispersion. A study of the variations of the chronaxie when the nerve is exposed to a known coagulating agent will give a trustworthy answer to this view.

The first experiment was carried out on the muscle-nerve preparation of the frog. The preparation was placed in a hard-rubber trough and the portion separating the chambers containing the muscle and the nerve was sealed off carefully with vaseline, so that solutions could be added to the nerve chamber without coming in contact with the muscle. Both chambers were then filled with Ringer's solution and the chronaxie of the nerve measured and found to be normal. Mercuric chloride was considered to be a good coagulating agent so one drop of a ten percent solution was added to the chamber containing the nerve. For the first fifteen minutes no change was noted in the chronaxie then suddenly there was a drop of 15-20% below normal. The next measurable value was about 20% above normal. The series of changes took place so rapidly that no more values could be obtained. The initial lag is explained by the slow penetration of the bichloride through the thick sheath of the nerve. The coagulating action of the mercuric chloride is so intense that the changes occur quite rapidly, nevertheless, in several repetitions of the experiment there can be no doubt that the chronaxie first decreases and then, later, increases above the normal value.

A milder coagulating agent was next tried, several drops of a ten percent solution of lead nitrate were added to the nerve chamber. Three or four minutes later the chronaxie was 22% below that of the initial normal value; eight minutes later 46% below normal, this was the minimum value. There was then a steady increase in the chronaxie, ten minutes later the chronaxie was only 16% below normal. A few minutes later the chronaxie was back to the normal level but this was only a pseudo-normal state for the rheobase was much higher than the normal rheobase. The chronaxie continued to increase until the nerve was paralyzed.

It would be of interest to study some organic coagulating agent and also study the changes that take place during recovery. In our study of the colloid chemistry of anesthesia we pointed out that under certain conditions the cell or tissue should pass back over in the reverse order the phenomena it exhibited when undergoing narcosis. The usual muscle-nerve preparation was used and the chronaxie of the nerve was found to be 0.075 micro-farad. Several drops of ethyl alcohol were then added to the nerve chamber and the changes in chronaxie were as follows: 0.068, 0.066, 0.077, 0.083, the preparation was narcotized two or three minutes after the last value was obtained. The solution in the nerve chamber was then removed with a pipette and fresh Ringer solution added; after allowing the solution to remain in the cell for a few minutes it was again replaced with fresh Ringer's and the recovery of the preparation awaited. The time of recovery naturally depends upon the reversibility of the coagulation produced, this in turn is a function of the concentration of the narcotic and the time exposure. For the experiment recorded here fifteen minutes passed before there were any indications of recovery; at the end of this period there were faint signs of twitchings with a potential of thirty volts.

The preparation was again washed with fresh Ringer's solution and the first value obtained was 0.087. Within the next ten minutes the chronaxie had dropped progressively down to 0.060 which was the minimum; from this time on there was a steady increase until the normal value was reached, the over-all time being about forty-five minutes. Throughout the experiment the nerve was washed frequently with fresh Ringer's solution. Thus there can be no doubt that the phenomena of recovery proceed in the reverse order to those of narcosis.

This phenomena of a decrease in chronaxie followed by an increase is not confined to the salts of the heavy metals and alcohol. Anesthetics such as ether do the same thing. In fact this property is so characteristic that in at least one case it has been proposed as a method of standardization for local anesthetics.

Chardot and Regnier[1] have shown that for cocaine hydrochloride solutions the final value of the diminution is a function of the concentration. They note that the phenomenon is reversible and that during the narcotization there in an elevation of the rheobase. The values obtained by them for the percentage depression of chronaxie with different concentrations of cocaine hydrochloride solutions, all at a pH of 6.8 are given in Table II.

TABLE II

% concentration	% depression	% concentration	% depression
0.05	63.	0.010	54.
0.03	62.	0.0075	43.
0.015	55.	0.0050	27.

Another interesting substance, urea, was found also to behave in the typical manner of first lowering then elevating the chronaxie. On washing the nerve with fresh Ringer solution the recovery was also typical in that the nerve passed through the stage of increased irritability (decreased chronaxie) before reaching the normal level. The decrease in chronaxie amounted to approximately 40% of the initial value.

The above cases are not isolated observations, other workers have noted similar changes in the chronaxie of a tissue when exposed to drugs. Thus Lapicque[2] noted that nicotine first decreases then later increases the chronaxie of the gastrocnemius muscle of the frog. S. Weisz[3] mentions several other cases. He found this effect for salts of mercury, arsenic, chromium, and manganese and also for carbon disulfide, ammonia, phosphoric acid, methyl alcohol benzene, aniline, and phenol. It is probable that the ammonia was converted into urea and was acting as such; this does not change the situation however, for we have shown that urea also behaves in the typical manner.

Before leaving this subject there is another interesting agent that is worth mentioning. The effect of X-rays on chronaxie have been investigated and

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[1] Soc. biol. de Paris, **78**, (2) 1247 (1926).

[2] Soc. biol. de Paris, **73**, (1) 654 (1921).

[3] Deut. med. Wochenschr., **55**, 782 (1929).

the results are quite interesting.[1] Wels found that X-rays can behave as coagulating agents for certain isolated proteins.[2] He also noted the changes in viscosity, first decreasing then increasing above the normal value, that are characteristic of certain protein sols when undergoing coagulation. Wels was unable to explain the initial decrease in viscosity, so thought that the first measurements might be in error.

X-rays are also able to coagulate the proteins of tissues. In connection with this Heilbrunn[3] says: "Williams was able to show very definite effects of X-ray treatment on the protoplasm of the stalk cells of *Saxifraga umbrosa*. Short exposures caused an increase in the rate of protoplasmic streaming, and also an increase in the Brownian movement of the small particles of the protoplasm. Longer exposures caused a diminution of the rate of streaming, and finally complete stoppage. Similar results were also recorded in an early paper of Lopriore. But this worker studied only the rate of streaming and not the Brownian movement. He found that a half hour treatment with X-rays caused an increase in the rate of streaming in the protoplasm of the leaves of *Vallisneria spiralis*. Treatment for an hour caused the protoplasm to become yellow, granular, and coarsely vacuolated. Seckt also found that short exposures to X-rays increase the rate of protoplasmic streaming in various plant cells and that longer exposures slow it. From all these results, it seems probable that X-rays first produce liquefaction, then coagulation of the protoplasm." The changes in viscosity noted above are typical of coagulating protoplasm.[4] The effect of X-rays is interesting in that they behave as coagulating agents but neither add nor subtract anything in the tissue.

From the previous discussion of the effects of coagulating agents or narcotics on the variations of the chronaxie, it would be expected that X-rays on short exposure would cause also an increase in the excitability, as a matter of fact this was found to be the case. The nerve-muscle preparation was exposed to X-rays (ten milliamperes at a distance of twelve inches) for short periods of time, the maximum time being thirty seconds. At first there was no change in the chronaxie, this was due to the fact that several minutes lapsed before the measurements were made. If the measurements were started immediately after the exposure, the chronaxie was 20-25% below normal and rapidly returns to the normal level, the time of recovery being about three minutes.

Thus from every angle the evidence is accumulating that any agent which causes a decrease in the dispersion of the nerve colloids will reproduce the phenomena of narcosis, which lends considerable credence to the colloid theory of narcosis.

Aside from the ability of this theory to account satisfactorily for the phenomena of narcosis, it is interesting in that it suggests the close relationship between stimulants and narcotics. Thus, as du Bois-Reymond concluded that the agent which gives rise to the excitation of the nerve is not

[1] Wilber: Unpublished Work.
[2] Archiv ges. Physiol., **199**, 226 (1923).
[3] Heilbrunn: Colloid Chemistry of Protoplasm, p. 138.
[4] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

the electrical current alone, but that it is due to the variations of the intensity of the current, one could best conclude that the phenomena of irritability are associated with the changes in dispersion of the colloids. For after all, the electrical current brings about an alteration of the dispersion of the colloids of the protoplasm. This was discovered by the physiologists themselves.[1] Heilbrunn,[2] after summarizing the literature on this subject, concludes that "for both plant and animal cells it seems certain that the passage of an electrical current very quickly produces a reversible gelation or coagulation of the protoplasm." Thus in regions of marked coagulation or peptization the phenomena of excitability are practically absent because it is very difficult to effect a change in dispersion. On the other hand, in a system that is undergoing a decrease in dispersion, as in narcosis, the decreasing stability of the system manifests itself in the phenomena of increased irritability.

Stimulants may be regarded as agents that initiate the change in dispersion of the colloids. According to the principles of thermodynamics, any process tends to occur if it is accompanied by a decrease in the free energy. The free energy of colloidal solutions is associated with the interfacial surface tension; so according to this rule colloidal systems have a tendency to coagulate, for by this process the active surface is diminished. It is not surprising then, to find that the change in dispersion brought about by drugs is usually associated with a decrease in dispersion or coagulation of the colloids of the biological system.

There are many interesting phenomena associated with the increasing excitability that is produced by coagulating agents. In another paper we have advanced the thesis that the increased excitability, if localized in certain tissues, may be associated with some of the phenomena of insanity.[3] One can see that, if the central nervous system was either directly or indirectly exposed continuously to coagulating agents, the tissue would be first stimulated then and later paralyzed, if the concentration of the coagulating agent were sufficiently great. The effects of the stimulation may easily be the bizarre mental reactions that are found in insanities caused by coagulating agents. Since we have already shown how the chronaxie of a nerve varies when exposed to lead salts, the following description, from Osler's "Modern Medicine," concerning the mental and nervous symptoms of lead poisoning are interesting. "There may be hysterical symptoms, 'toxic hysteria,' with hemianesthesias and other stigmata, or other hysterical outbreaks of excitement or convulsions, especially in predisposed young women.

"The most common and striking cerebral symptoms are epileptiform convulsions, mania, delirium, and coma; sometimes a picture more or less closely resembling paretic dementia. The outbreak often comes suddenly; alcoholics are especially liable. Convulsions, or less commonly delirium, usually occur first. The convulsive attacks are epileptiform with clonic and tonic movements; only one may occur, but, as a rule, the attacks are repeated at varying

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[1] Bayliss: Proc. Roy. Soc., **91B**, 196 (1920).

[2] "Colloid Chemistry of Protoplasm" (1928).

[3] J. Phys. Chem., **35**, 1606 (1931).

intervals over days—rarely, even weeks. Delusions of persecution and particularly hallucinations, especially of terrifying character, are common; though they are not confined to such subjects, hallucinations are very frequent in those who are also alcoholic, and with marked tremor the resemblance to delirium tremens may be very striking. . . . Most important of all the nervous symptoms is paralysis; in its usual distribution it is of itself almost distinctive of lead poisoning. When typical it produces so-called 'wrist-drop' and 'toe-drop,' which is bilateral."

Weisz[1] studied the effect of heavy metals on the chronaxie and found that there was an initial decrease which passed through a point of inflection and then went above normal. He tried the interesting experiment of giving guinea pigs very small amounts of the salts over a period of several days and measuring the chronaxie in the animal every day. He found that the phase of decreased chronaxie corresponded with the increased irritability of the animals and the increasing chronaxie ran parallel with the paralysis.

The variations of the chronaxie of a tissue caused by a decrease in dispersion of the bio-colloids, present another type of curarization that is very interesting from a theoretical viewpoint. If the chronaxie of the nerve and muscle are not the same within the two to one ratio the nerve impulse will not affect the muscle. The cases of curarization, mentioned above, involved the change, increase or decrease, of either the muscle or nerve separately. From our study it is clear that the chronaxie can be either decreased or increased, depending upon the concentration of the drug; or, if the concentration is high, the time of action. Thus if a single drug brought about these variations of the chronaxies of both the muscle and nerve but at different rates in the two tissues one would have the interesting case of a drug antagonizing itself. If the drug would first decrease and then increase the muscle chronaxie, for example, above twice its normal value while the nerve was only in the phase of decreasing chronaxie, a state of heterochronism would exist and paralysis would result. Now if one bathed the nerve in higher concentrations of the same drug, or allowed a longer time of action, if the concentration was sufficiently great, the chronaxie of the nerve would also pass through a point of inflection and rise above normal; as soon as the nerve chronaxie increased to that of the muscle a state of isochronism would again exist and the paralysis disappear. This interesting case of "autoantagonism" has not been realized to the best of our knowledge, nevertheless the existence of such cases is probable and unless one knew of the variations of the chronaxie the explanation would be perplexing.

In summarizing, the situation is briefly that the physiological phenomena that an isolated tissue exhibits when undergoing narcosis can be accurately followed by measuring the alterations in the chronaxie. The first effect of the narcotic is to increase the excitability of the tissue; the second effect is for the excitability to pass through a maximum value, then decrease below normal. The very interesting thing is that indisputable coagulating agents, such as the

[1] Deut. med. Wochenschr., 55, 782 (1929).

salts of the heavy metals, in so far as they affect the tissue, faithfully reproduce the same phenomena. The correspondence between the behavior of known coagulating agents and narcotics is so close that one is drawn to the conclusion, which has also been reached from independent chemical sources, that coagulation and narcosis go hand in hand.

In presenting the colloid theory of narcosis in which coagulation, or decrease in dispersion, of the bio-colloids was the important point, it was a matter of interest to know which type of bio-colloids were undergoing the decrease in dispersion. From the inability of the lipoid theory to account for the phenomena of narcosis, except in the most elementary cases, we were led to postulate that if the lipoids had any rôle in narcosis it was of secondary importance and that the proteins of the system were the important colloids to be considered. The physiological evidence, based on a study of the chronaxie, is also in harmony with this view.

In the measurement of the variations of the chronaxie in a changing environment, one has a method of indirect analysis, which, if properly interpreted, will give some idea of the chemical nature of the irritable substance in the nerve. The method that is proposed is based upon the following phenomenon: If the pH of a protein sol is changed from a high value to that of a low value the degree of dispersion of the sol is greatly affected. There is, in general, a small range in the pH scale in which the degree of dispersion is much less than that at any other value, this region being termed the iso-electric point; on either side of the iso-electric point the dispersion becomes greater. For proteins the iso-electric points are quite characteristic, but for lipoids the case is different. If iso-electric points exist at all for lipoids, they are not of sufficient importance to be recorded in the literature and are certainly not characteristic.

From the discussion above of the variation of the chronaxie of a tissue whose colloids are undergoing a decrease in dispersion, we would conclude that in a medium of varying pH the final chronaxies would be at a maximum at the iso-electric point, or that the chronaxie would pass through a maximum at a pH which would be within a reasonable range of that of other proteins whose iso-electric point are known. On the basis of the lipoid theory nothing but general confusion can be predicted.

The above experiment of varying the pH of the medium surrounding the nerve and determining the chronaxie as a function of the hydrogen ion concentration was carried out. A series of buffer solutions of disodium phosphate and citric acid whose range varied from a pH of 2.2 to 8 were prepared. The muscle-nerve preparation was placed in the hard rubber chamber and the partition separating the muscle from the nerve was well sealed off with vaseline so that the buffers could be added to the nerve chamber without coming in contact with the muscle. The alkaline buffers were added first. After the addition of each buffer three or more determinations of the chronaxie were made. The buffer was then removed from the chamber and the nerve washed with fresh Ringer solution, then the next buffer was added. The results of the experiments are summarized in Table III.

TABLE III

pH	Average value of the chronaxie	pH	Average value of the chronaxie
2.2	0.057	5.0	0.113
3.0	0.063	6.0	0.073
4.0	0.089	7.0	0.067

There can be little doubt about the chronaxie passing through a well-defined maximum. If the results are plotted graphically, the maximum is found to be at approximately a pH of 4.8. That is, the iso-electric point of the proteins that are responsible for the excitability is at pH 4.8. This value of the iso-electric point is within the range that is commonly found for many proteins. The following values taken from Lloyd, "Chemistry of the Proteins" are interesting in this connection, Table IV.

TABLE IV

Protein	pH	Protein	pH
Cryst. egg albumin	4.8	Collagen	4.8
Serum albumin	4.7	Serum globulin	5.5
Gelatine	4.7-5.5	Myogen (frog)	6.0

Lapicque and Larrier[1] in an analogous manner have studied the variations of the chronaxie of the muscle at different hydrogen ion concentrations. They found that in the neighborhood of pH 4 the chronaxie reached a maximum. They also found the same value for the heart muscle of the frog. The iso-electric points of the irritable substances of the muscle and nerve are so close together that one wonders whether the same material is not responsible for the excitability of both the muscle and nerve. The iso-electric point of the proteins of the muscle as measured by the swelling have been found to be at a pH of 4.8.[2] Another interesting feature of the data of Lapicque and Larrier, which they fail to emphasize, is that they found a second maximum in the chronaxie at a pH of 6. A protein can be extracted from muscle, which is commonly called myogen; the myogen from frog's muscle has an iso-electric point at a pH of 6.0. Thus there appear to be two irritable proteins in frog muscle. It is also possible that with smaller changes in pH more than one point of inflection may be found for the nerve.

An experiment was carried out using substances other than hydrogen and hydroxyl ions as the coagulating and peptizing agents. While the experiment was not successful it is of sufficient interest to be included within this report. A dilute solution of alcohol was placed in the medium surrounding the nerve and the chronaxie followed until the tissue was narcotized. The alcohol solution was then removed and the nerve bathed in a solution of sodium thiocyanate; as this substance is an excellent peptizing agent it was

[1] Soc. biol. de Paris, **78**, (2) 450 (1926).
[2] Archivio de Scienze Biol., **5**, (1924).

hoped that it would repeptize the coagulated proteins of the nerve. In the several experiments carried out with the bromides, iodides, and thiocyanates no acceleration in the rate of recovery was noted. A possible explanation of this result is that the ions do not readily penetrate the thick myelin sheath of the nerve.

This explanation was tested in the following way, a nerve was narcotized by treatment with lead nitrate, the narcotized nerve was then bathed in a dilute solution of sodium iodide. If the iodide ion penetrates into the interior of the nerve it would produce the insoluble lead iodide, and the removal of the lead ions would lead to an improvement in the condition of the nerve, which can be followed by measuring the chronaxie. In the experiment that was tried there was no change in the chronaxie, which apparently means that the iodide did not penetrate into the nerve. In confirmation of this view was the fact that the lead iodide appeared, to the unaided eye, to be deposited only upon the surface of the nerve.

The sluggish penetration of these ions led us to assume that if any ions would be permeable it would be the hydrogen and hydroxyl ions. The above work on chronaxie and pH confirms this.

In conclusion, one can rest assured that the lipoids play a secondary role relative to the proteins in the cell. There are some proteins which are intimately associated with the phenomena of irritability or narcosis; and when these protein sols undergo a decrease in dispersion the tissue undergoes a typical narcosis.

Summary

1. A brief review of the concept of chronaxie and its applications to the problems of drug action is given.

2. In narcosis, the tissue first becomes more excitable then normal, then gradually becomes less excitable.

3. The measurements of the chronaxie of a tissue when it is undergoing narcosis reveal that the chronaxie also changes in the characteristic manner of first decreasing and then increasing above normal.

4. When tissues are treated with indisputable coagulating agents such as salts of lead and mercury the changes in chronaxie are identical with those produced by narcotics. This lends credence to the view that narcotics are substances which are capable of causing a decrease in dispersion of the cell colloids.

5. It is a matter of interest to know what type of colloids are undergoing a decrease in dispersion in narcosis. The measurement of the chronaxie with varying pH is a possible method of indirect analysis, in that it will differentiate between lipoid and protein substances if either is associated with the phenomena of excitability; the proteins have characteristic iso-electric points whereas the lipoids do not.

6. If protein colloids are responsible for the irritability, then, according to the colloid theory of narcosis, the irritability should be at a minimum at the iso-electric point of the protein.

7. Chronaxie measurements show that the excitability of the frog's nerve is at a minimum at a pH of 4.8. The excitability of the muscle shows two points of inflection. The iso-electric point of pH 4 corresponds roughly to the iso-electric point of the muscle proteins as found by swelling at pH 4.8. The second iso-electric point of pH 6 is identical with that of the muscle protein called myogen.

Cornell University.

THE PHYSICAL CHEMISTRY OF BACTERIAL AGGLUTINATION AND ITS RELATION TO COLLOIDAL THEORY*

BY STUART MUDD, R. L. NUGENT AND L. T. BULLOCK

Bacteria, in addition to their obvious medical and industrial importance, offer to the colloid chemist for study relatively reproducible suspensions of a great variety of chemical and physical properties. Although much of this rich field for investigation remains little explored, certain aspects, notably those relating to the stability of bacterial suspensions, have received intensive study. The purpose of the present paper is two-fold: first, to attempt a more nearly satisfactory analysis than is at present available of the physical chemical factors determining the stability of bacterial suspensions, and, second, to offer, regarding the general theory of colloidal aggregation, certain suggestions derived from analysis of these special cases.

The aggregation of bacteria under the action of specific substances in the blood of infected man or animal is a special manifestation of the defensive reactions upon which higher animal life depends. The mechanism of this aggregation has received particularly intensive study. We shall try to reach conclusions regarding the general problem of colloidal aggregation through following in outline the history of the study of this special type of aggregation.

The fact that the phenomena of bacteriology and immunity have been described in a special terminology has been a serious obstacle to the much needed collaboration of chemists in these problems. Let us therefore begin by defining our terms. A foreign substance, which may be a component of a bacterium or other cell or a pure foreign protein, is called an *antigen* if when introduced into the blood stream it gives rise to a corresponding "immune" substance called *antibody*. The liquid part of the blood which is extruded from a contracted blood clot is known as the *serum*, and if it contains specific antibodies it is known as an *antiserum*. The antibodies are designated in terms of the phenomena they bring about by interaction with their corresponding antigens. Thus an antigen in solution may be precipitated by its corresponding antibody, which is then called a *precipitin*. If the antigen is a component of a bacterium or other foreign cell, interaction with antibody may lead to aggregation of the foreign cells; this aggregation is known as *agglutination*, and the antibody involved is called an *agglutinin*.

There is good reason to believe that agglutinins and precipitins may be the same substances merely reacting with antigen under different circumstances.[1] Thus the antiserum formed by injection of animals with crystalline egg albumin precipitates the egg albumin from solution. If, however, the antiserum reacts with egg albumin which has first been adsorbed on collodion particles, these particles are agglutinated.[2] If now these same agglutinated

particles are allowed to come into contact with white blood cells the particles are taken within the white cells.[3] There is thus strong evidence to indicate that the reaction between antibody and antigen is the essential process which leads to various important secondary phenomena among which are included precipitation, agglutination and the ingestion and destruction of the antigen by the defensive cells of the body. A bacterium or other cell which has combined with antibody is said to be *sensitized*.

Agglutination by antibodies was described by Gruber and Durham in 1896 and precipitation by Kraus in 1897. The great importance of the phenomena soon became apparent and led to the attempt to discover the mechanism by which antibodies act. Two opposing schools developed. The line of cleavage was between the points of view of structural organic chemistry and of colloidal chemistry. Ehrlich and the German school built up the elaborate side-chain theory of immunity. Agglutinins according to this theory possessed certain chemical groupings (haptophores) by virtue of which they combined specifically with their corresponding antigens; other chemical groupings or side chains (agglutinophores) were supposed to bring about the agglutination.

In opposition to the highly elaborated structural chemical side-chain theory, Bordet and the French school postulated a relatively simple colloid-chemical mechanism. "Bordet[4] made the important observation that *agglutination does not occur if both the bacterial suspension and the agglutinating serum are dialyzed free from salts before mixing*; but if, to such mixtures, a small amount of NaCl is added, agglutination and precipitation of the bacteria occur at once (Reference 1, p. 156). This observation brought the phenomenon of bacterial agglutination into close relation with the precipitation of colloids by electrolytes, Bordet comparing it to the precipitation of particles of inorganic matter suspended in the fresh water of rivers that occurs when the fresh water meets the salt water of the ocean. He found that if the agglutinin combined with the bacteria in the absence of the salts, the resulting compound was precipitated by the addition of minute amounts of electrolytes, which alone did not precipitate or agglutinate the bacteria or the serum. This is a general principle applying not only to the agglutination of bacteria, but also of other cells."[5]

Thus in agglutination by antibodies there are two separable stages, the combination of antigen and antibody, and the subsequent aggregation of the antigen-antibody complex. According to the German school both the combination of antigen and antibody and the subsequent agglutination occurred by virtue of special chemical groupings. According to the French school the combination of antigen and antibody was an adsorption and the subsequent agglutination occurred according to the ordinary rules of colloidal aggregation. The gifted supporters of these conflicting theories and their followers vigorously sought experimental verification, and a wealth of data has accumulated. Only within recent years, however, has it become apparent that each view contained a part and only a part of the truth.

Without attempting to discuss in detail the combination of antigen and antibody we may state categorically the now generally accepted conclusion

that this combination depends upon specific chemical constitution and that the specifically reacting groups may constitute only a very small part of the molecules. Recent work has demonstrated indeed that the specificity of combination between antigen and antibody may be determined by the spatial configurations about a single carbon atom. Thus Landsteiner and van der Scheer[6] have prepared antigens containing the acyl radicals of the levo-, dextro-, and meso-tartaric acids. Injection of these antigens elicited antibodies which combined specifically with the respective levo-, dextro-, and meso-stereoisomers. Avery and Goebel[7] have similarly prepared antigens by coupling proteins with p-aminophenol β-glucoside and p-aminophenol β-galactoside. Injected into rabbits, antibodies were elicited which reacted specifically with the particular hexoside contained in the injected material. Specificity of combination in this case was determined by the stereochemical configuration of the hexoside, and was independent of the protein to which it was coupled. A detailed discussion of immunological specificity may be found in Wells': "Chemical Aspects of Immunity."[1]

What, then, is the mechanism by which the specific chemical combination of antibody with antigen is able to bring about agglutination? We will first summarize the objective alterations in physical chemical properties resulting from combination with antibody. These have been worked out by Bordet, Bechhold, Porges, Coulter, Northrop and De Kruif, Northrop and Freund, Shibley, Mudd and Mudd, Eagle, and Mudd, Lucké, McCutcheon and Strumia. With these data before us, we will discuss earlier experiments and theories, and will finally attempt a more nearly adequate treatment than is at present available.

Various bacteria vary widely in the chemical composition and colloidal properties of their surfaces. Thus virulent pneumococci possess capsules composed largely of certain complex polysaccharides;[8] in the "rough" variants of pneumococci these carbohydrates are lacking and the surfaces are chiefly protein. Certain bacteria isolated from tuberculosis of birds or of cold-blooded animals behave as though their surfaces were largely lipoid.[9] In an oil-water interface most bacteria show decided preferential wetting by the aqueous phase; many "acid-fast" bacteria under the same circumstances are wet preferentially by the oil.[9,10] Certain microorganisms have definite isoelectric points; others retain a negative surface p.d. even down to pH values below 2.0; we have cultures of at least three strains of "intestinal" bacteria which show only a minimal surface p.d. in buffers of any pH studied. Some bacteria readily form stable suspensions; others may be suspended only with difficulty and undergo spontaneous aggregation.

Interaction of these bacteria each with its corresponding specific immune serum masks this great diversity. As the bacteria combine with progressive concentrations of their corresponding immune sera, their surface properties progressively converge toward a new and common set of surface properties.

This convergence for the isoelectric points is shown in Fig. 1. Each bacterium used (except S. pullorum) had been isolated from a human patient; the bacterial suspension was allowed to stand overnight in contact with serial

dilutions of the serum of that patient.* Appropriate controls showed that the resulting combinations with antibody were specific. The sensitized bacteria were washed in 0.85% NaCl solution and their isoelectric points were determined in acetate buffer series with the aid of a Northrop-Kunitz microcataphoresis cell.[12] Before sensitization the staphylococcus retained a negative
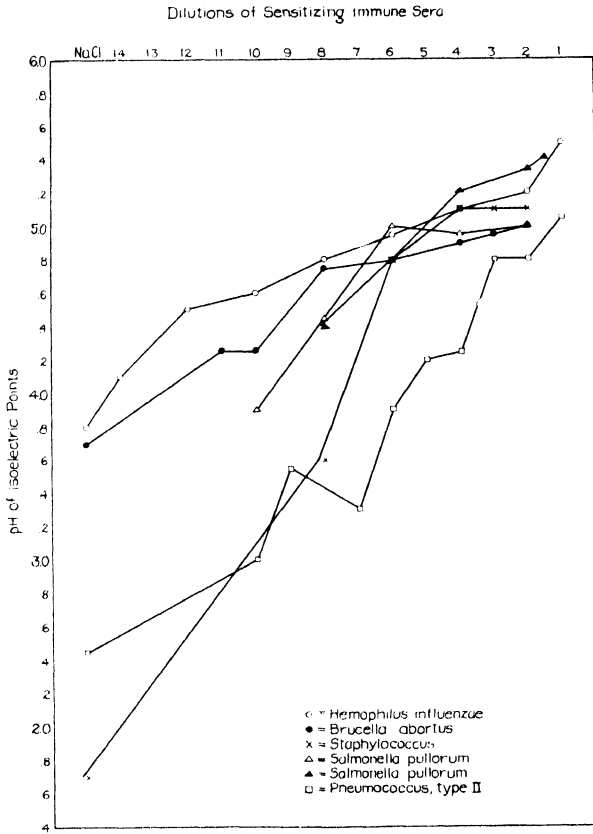
FIG. 1

Convergence of isoelectric points of various bacteria specifically sensitized with human immune sera. Abscissae are the final dilutions of immune sera in 0.85% NaCl solution used to sensitize the bacteria. These are expressed as powers of 2; thus 5 indicates a dilution of 2^5 or 1 volume of serum diluted to 32 volumes with NaCl solution. Ordinates are the isoelectric points of the sensitized, washed bacteria as determined in a microcataphoresis cell. As the concentration of sensitizing serum increases the diverse isoelectric points shift to maximal values of pH 5.0 to 5.5, thus approximating the isoelectric point of serum globulin.

charge even in N/100 HCl, the pneumococcus was isoelectric between pH 2.0 and 3.0 and H. influenzae and B. abortus between pH 3.0 and 4.0 and S. pullorum had little if any surface p.d. in any buffer used. With progressive sensitization the isoelectric points of all the bacteria shifted progressively until values of pH 5.0 to 5.5 were reached.

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* S. pullorum was sensitized with the sera of typhoid fever patients, with which S. pullorum interacts specifically.[11]

Concomitant with this convergence of isoelectric points with progressive sensitization, there is a convergence of other surface properties. The surface p.d.'s change to a common value, usually lower but in some cases higher than the unsensitized value.[13] The wetting properties, which may have been hydrophilic or hydrophobic in the unsensitized state, become those of protein.[14] The cohesiveness of the sensitized bacteria becomes great. Concomitantly also with these changes in surface properties there occurs the agglutination which has been discussed. The extensive data on which these summary statements are based may be found in references 3, 13 and 15, and in earlier works there referred to.

The explanation of this convergence of surface properties, as is no doubt evident, is that the antibodies which combine with the antigens of the various bacteria or other cells form deposits or films, which do not differ greatly one from another, on the antigen surfaces. The properties of these films are similar to those of denatured serum globulin,[13,14] but not, at least in some cases, identical with them.[3,16] It is probable that the antibody is itself a modified serum globulin or at least contains serum globulin as a constituent part. The most noteworthy difference of the antibody-globulin from normal serum globulin is the specific combining affinity of the antibody for antigen. The sensitized surface has in addition to the properties already described the property of adsorbing non-specific globulin and albumin (complement) from the serum.[17] The final surface thus built up upon the antigen is thus probably a composite film, composed of antibody-globulin specifically combined with the antigen and more or less adsorbed non-specific serum protein. Specific serum sensitization thus makes many chemically diverse particles essentially similar in their surface properties and markedly increases their tendency to agglutinate. From the point of view of immunity the important fact is that this sensitization process renders the foreign particles susceptible to ingestion (phagocytosis) by the defensive cells of the body; however, ingestion by cells is not within the scope of the present paper. This arrangement, by which many diverse substances are given a common set of properties that can in the main be dealt with successfully in the body, were it the product of human intelligence, would be an extremely ingenious solution of a difficult chemical problem.

With these recent data with regard to the sensitizing antibody film before us let us return to consideration of such earlier experiments and theories as throw light upon the physical chemical factors affecting the stability of suspensions either of unsensitized bacteria, sensitized bacteria or of both. The basic discovery of Bordet that sensitized bacteria are stable in distilled water but are agglutinated by traces of electrolyte was extended by Bechhold in 1904.[18] Bechhold showed that the cation was the important precipitating ion and that its efficiency increased rapidly with valence. The bacteria studied by Bechhold, i.e. typhoid and dysentery bacilli and staphylococci, with respect to precipitation by electrolytes resembled emulsoid colloids; after sensitization by specific serum they behaved more nearly like suspensoids. These general results were confirmed and extended by many investigators.

Tulloch[19] concluded in 1914 that "as unsensitized organisms behave—towards electrolytes as does fresh egg protein, but when sensitized have characters that recall those of denatured egg-white, the process of sensitization is akin to that of denaturation."

Buchanan[20] in 1918, devoting his presidential address before the Society of American Bacteriologists to the subject of bacterial agglutination, reviewed the earlier work and proposed his own theory of the stability of bacterial suspensions. Buchanan regarded the negative *charge* as the stabilizing factor and *"surface tension"* as the aggregating factor. "We may regard the similar electric charge as constituting the repulsing agency, the surface tension as the attracting agency. A study of the agglutination phenomenon then resolves itself into a consideration of the means whereby these two forces may be modified, increased or diminished. Agglutination occurs whenever the similar electric charges are decreased to amounts such that they will no longer overcome the pull of surface tension. Or conversely, surface tension may be increased until it overcomes the dispersion effect of the similar charges."*

Herzfeld and Klinger[23] about the same time attributed the stability of bacterial suspensions to the water-solubility ("Hydrophilie") of the surfaces due to adsorption of soluble decomposition products. Electric charge according to Herzfeld and Klinger played only a subordinate part.

The work of Northrop and De Kruif[24,25] and Northrop and Freund[26] marked an important advance in this field. Their studies were of peculiar importance for at least two reasons: firstly, that they substituted measurement of the physical factors involved for speculation about them, and secondly that they laid the foundation upon which the modern conception of the sensitizing antibody-protein surface film has been established.

The *electrokinetic p.d.* was calculated in this work from direct measurements in an improved microcataphoresis cell. Bacteria were dried in thick films upon plane glass surfaces; these were immersed in aqueous solutions of various salt contents, were allowed to cohere, and the force required to separate them was determined by a du Noüy tensiometer. The relative *cohesion* between bacteria in various suspending solutions was thus measured.

Bacteria in electrolyte solutions of .001 M concentration or less were found to be stable if the electrokinetic p.d. exceeded the critical value of $\pm$ 15 millivolts. The critical potential for unsensitized red blood cells was about $\pm$ 6 millivolts, for sensitized red blood cells about $\pm$ 12 millivolts. Within these critical zones both types of cell aggregated when the electrolyte content of the medium was low. At higher concentrations of electrolytes, .01 M to 0.1 M, aggregation sometimes occurred within the critical potential zones, sometimes did not. In salt concentrations exceeding 0.1 M aggregation rarely occurred even though the electrokinetic p.d. was reduced to zero. Bacteria

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* Surface p.d. or electrokinetic p.d. and surface "charge" are both manifestations of the existence of an electrical double layer at the particle-dispersion medium interface. The direct stabilizing action of the electrical double layer is believed to be due to the mutual repulsion of similarly charged surfaces.[21] The electrokinetic potential difference is proportional to the surface charge[22] and since it is the measurable factor, it will hereinafter be frequently referred to as the stabilizing influence.

sensitized with immune serum were regularly agglutinated when the p.d. was brought within the critical limits regardless of salt concentration.

Measurement of cohesive force between the unsensitized bacteria showed progressive reduction with increasing electrolyte concentration. Over the range of concentration of 10⁻⁴N to N this reduction in cohesive force between unsensitized bacteria amounted to approximately 50%, according to the figures of Northrop and De Kruif. The cohesion of bacteria sensitized with immune serum was high and was not affected by salt concentration.

These results were summarized by Northrop and De Kruif in part as follows: "Electrolytes in low concentration, (0.01 N), affect primarily the potential, and in high concentration decrease the cohesive force.

"As long as the cohesive force is not affected, agglutination occurs whenever the potential is reduced below about 15 millivolts.

"When the cohesive force is decreased the critical potential is also decreased, and in concentrated salt solution no agglutination occurs even though there is no measurable potential.

"The addition of immune serum prevents the salt from decreasing the cohesive force between the organisms, and agglutination therefore is determined solely by the potential, provided excess immune body is present. Whenever the potential is decreased below 15 millivolts the suspension aggregates."

This work leaves little doubt that the electrokinetic p.d. is a major factor in the stability of bacteria as of other colloidal suspensions. It provides definite quantitative evidence also that cohesion is a factor of major importance. Ordinary bacteriological experience affords sufficient confirmation of the importance of cohesion. For instance young glycerol-agar cultures of a certain acid-fast bacterium, Mycobacterium chelonei, (turtle bacillus), form even and stable suspensions with ease when shaken up in salt solution. The same cultures, aged and somewhat dried out, it may be impossible to suspend uniformly, even with the aid of much grinding and shaking. Further confirmation is yielded by the "resuspension" and "interfacial" methods which afford direct, although only semi-quantitative, evidence of the cohesion of bacterial clumps when subjected to shaking and to the dispersing action of an oil-water interface. Hundreds of such observations have shown that sensitized bacteria are much more cohesive than the same bacteria before sensitization.

Since the work of Northrop and de Kruif, Kruyt[27] and his associates at the van't Hoff laboratory in Utrecht have in recent years made extensive studies of emulsoid colloids. The hydration of the disperse phase is estimated from careful viscosity measurements, and the p.d. by cataphoresis. These studies have demonstrated two major stabilizing factors for hydrophile systems, *electrokinetic p.d.* and *hydration*. If the disperse phase is dehydrated by alcohol or acetone stabilization depends, as in suspensoid systems, principally upon charge. It is obviously necessary to include this unquestioned influence of hydration in any completed theory of bacterial agglutination.

The studies of dehydration by tannin made by Bungenberg de Jong in Kruyt's laboratory are of especial interest for our purpose. Carbohydrate or protein emulsoids are given by tannin the properties of suspensoids. This action was explained in an early paper by de Jong[28] as follows:

"We suppose that here the dehydration is a phenomenon caused by the adsorption of the tannin on the lyophilic particles, by which the residual affinities, which otherwise bind the water of hydration, become partially neutralized by the tannin; the tannin on the other hand does not bind any water, but removes it from the particles. . . .

"Perhaps the theory of Langmuir-Harkins may give us insight into the direct cause of this dehydration. The tannin will be adsorbed in an orientated state. With the colloid carbohydrates the glucose side of the tannin molecule will direct itself towards the surface of the sol particles, i.e. inwardly. The phenol groups of the digallic acid residues will be directed towards the external phase. Now the surface of contact of the sol particles consists of a great number of feebly lyophilic phenol groups. Also, with the adsorption on proteins we are to suppose, that the phenolic groups in tannin adsorbed are outwardly directed, so that there is no more opportunity for important hydrations."

The important thing is that surface films of tannin are bound around protein particles. The tannin surfaces are not hydrophilic. The stabilizing action of hydration is thus lacking and the particles aggregate.

Similar,[29] though quantitatively less, dehydration could be brought about by synthetic tannins and by simpler polyphenols. The dehydration of protein sols is relatively greatest at the isoelectric point. The dehydrating power increases rapidly with the number of phenolic groups in the molecule, although simultaneously other influences help to determine the dehydrating power.

Later work[30,31] afforded evidence of a definite separation of a tannin- or polyphenol-rich liquid phase about the surface of the particle. "The dehydration is attributed to an actual phase boundary between the adsorbed tannin-rich layer and the tannin-poor dispersion medium." However this may be, work in this laboratory has shown evidence of the building up of an adsorption film on particles exposed to increasing concentrations of tannin and then washed. This work will be described in more detail later.

The results obtained by Kruyt, de Jong and others working in Kruyt's laboratory have clearly demonstrated that the question of the state of hydration of surfaces is a factor of major importance and must be dealt with in any general consideration of the agglutination of bacteria. These conceptions have been applied to serology by Reiner and his associates. They have made an important contribution to serology by demonstrating that precipitation, agglutination,[32] adsorption of complement[33] and the preliminary steps leading to lysis[32] and to ingestion by white blood cells[34] could all be brought about by treatment of cells with tannin. Thus the effects of antibodies were imitated in a striking manner by a substance of less complex chemical constitution. These results have been confirmed and extended by Freund[35] and by Neufeld and Etinger-Tulczynska.[36]

On the basis of the similarity of these effects of tannin and antibodies Reiner has advanced a "dehydration" theory of antibody action. Reiner's theoretical treatment of aggregation[32] we believe to be unsound for reasons that will be set forth in more detail later. Moreover, whereas Reiner's contribution in bringing the importance of hydration to the attention of serologists is apparent, the justification for singling out hydration in this way from among the several controlling physical factors, is by no means apparent. In fact we find no justification which seems to us adequate, theoretically or empirically, either in Reiner's papers or our own work.

A brief description has now been given of some of the more important general discussions of bacterial agglutination, which have appeared up to the present time. These discussions apply both to unsensitized and to sensitized bacteria. Buchanan's discussion on the basis of charge and surface tension, fails to include a discussion of the importance of hydration of bacterial surfaces. Northrop and De Kruif confirmed the importance of surface charge on the basis of quantitative measurements and demonstrated that a second factor must be taken into account, which they call "cohesive force." Their method of measuring "cohesive force" has been described. They were not inclined to identify it with surface tension.[37] It is apparent that they too do not fully discuss the question of surface hydration.

Reiner insists on good grounds that surface hydration must be considered as a factor of major importance in the agglutination of sensitized bacteria. He believes that he has been able to formulate the general question of the stability of bacterial suspensions in terms of the "attraction" of the bacteria which he defines in terms of free surface energies. The views of both Northrop and De Kruif and of Reiner are widely quoted.

It is apparent that no writer on bacterial agglutination to date has properly defined the interrelationship of surface tension, cohesion, hydration, and surface charge, as affecting the stability of suspensions either of unsensitized or of sensitized bacteria. Further, so far as has been ascertained, no writer on pure colloid chemistry has described this interrelationship in such a way that it may be directly applied to the question of bacterial aggregation.

In the remaining portion of this paper, it is therefore proposed first to discuss in so far as necessary, the general question of the factors affecting the stability of suspensions of colloidal particles, and then to discuss the stability of suspensions of unsensitized and of sensitized bacteria on the basis of previous work, the theoretical discussion to be presented here and of experimental observations made in connection with the preparation of the present paper. It is found that certain implications, new even in general colloidal theory, emerge from this process.

The Stability of Dispersions of Colloidal Particles in Water and Aqueous Solutions

The purposes of the present paper do not require an exhaustive treatment of the subject of the aggregation of colloidal particles, but rather a working outline of the subject to use as a basis for the consideration of those phenomena

of bacterial aggregation which are of importance in bacteriology and immunology.

There are two necessary conditions for the existence of a stable dispersion of colloidal particles in an aqueous medium. The first is that the mass and size of the particles be small enough so that they remain suspended for the period under consideration against the force of gravity.[38] The second is that some factor must operate to prevent the aggregation of the particles to form larger masses which would no longer remain suspended.[39]

The mass and specific gravity of bacteria is such that if no appreciable aggregation occurs, the amount of settling which takes place in eighteen hours is sufficiently small to be neglected. For this length of time therefore, bacterial suspensions may be treated as suspensions of colloidal particles. This fact is important, because the agglutination phenomena which are important in bacteriology and immunology ordinarily take place within eighteen hours. The first necessary condition for the existence of a stable suspension of particles is met by suspensions of single bacteria and therefore need not be further discussed here.

Given a dispersion of particles in water whose mass and size are sufficiently small so that settling is slow, three general factors must be considered as determining whether or not appreciable aggregation of the particles takes place within a given period of time.[40] The first condition requisite to the aggregation of particles is that their Brownian motion must bring them into contact with one another. Therefore the first general factor which must be considered is the rate at which Brownian motion tends to bring this about. The major experimental factors affecting this rate are the concentration, or number of particles per unit volume of the dispersion, the mass and size of the particles, the viscosity and the temperature of the suspension.[41] The study of variation in these factors upon the rate of agglutination of bacteria is of theoretical interest. However the observations of the agglutination of bacteria which are of direct importance in bacteriology and immunology are made under fairly constant conditions, so far as these factors are concerned. These usual conditions are such that the expectation of collision due to Brownian motion in the absence of repelling force is sufficient to cause rapid, complete aggregation of the bacteria if each opportunity for collision results in contact of the particles, and each contact results in cohesion. For these two reasons further discussion of the effect of variation in factors which affect the rate of opportunity for collision due to Brownian motion is unnecessary, from the point of view of the purposes of the present paper. Complete discussion may be found in comprehensive treatises on colloid chemistry.[42] Northrop has discussed these factors in relation to bacterial agglutination.[15]

The second general factor which must be considered as determining whether or not appreciable aggregation of colloidal particles will take place within a given length of time is the probability of contact when opportunity for collision is provided in consequence of Brownian motion. It is clear that such contact must occur unless prevented by some repelling force acting between two particles tending to collide in virtue of their Brownian motion.

If this repelling force is sufficient to overcome the momentum of the particles contact will not occur. There must obviously be a value of any such repelling force at which it just balances the momentum of the particles. This may be called the critical value of the force in any case.

The critical value described is strictly applicable only to a single pair of particles tending to collide under given conditions. In any system of dispersed particles, there is a statistical distribution of velocities due to Brownian motion.[43] Therefore a given repelling force may prevent certain collisions and not others in any given case. The critical value of the repelling force for a system of dispersed particles is therefore the value which is just sufficient to prevent a sufficient majority of contacts from taking place when opportunity is offered for collision.

The third general factor is the probability of cohesion after contact has been made. The interface between a dispersed particle and its dispersion medium is the seat of free surface energy equal to the free interfacial energy per unit area multiplied by the surface area of the particle. Contact of two particles results in a decrease in free surface energy* equal to twice the area of contact of the particles, times the interfacial tension, or:

$$\triangle F = 2 S \gamma AB$$

where $\triangle F$ is the decrease in free surface energy, S is the area of contact of the two particles in contact and γAB is the free interfacial energy per unit area.

Following Harkins'[44] general treatment of work of cohesion, it is apparent that the work of cohesion between two such particles in contact is measured by the free energy increase necessarily attendant upon their separation under ideal conditions**, or:

$$Wc = 2 S \gamma AB$$

where Wc is the "work of cohesion" and the other symbols have the same significance as before.

In order to cause separation after contact has been made, the dispersive forces† must provide a minimum energy equal to Wc. If Wc is greater than

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* The free interfacial energy as considered here involves any effects due to the existence of an electrical double layer at the particle-dispersion medium interface. It is a composite result of the interaction of three sets of force fields, those of the particle molecules, those of the disperison medium molecules and ions and that due to the existence of the aforementioned double-layer. No assumption is necessary here, and none is made as to the equality of the interfacial tension at the micro-particle-dispersion medium interface referred to and the interfacial tension at a macro-interface between the dispersion medium and the material of which the particles are composed.

** The question of the separation of particles under non-ideal conditions will be discussed later in connection with Figs. 4, 5, 6 and 7.

† Exact definition of these dispersive forces is difficult or impossible. It seems, however, that at least three factors may be recognized in a qualitative way:

(1) The Brownian motion itself.

(2) Electrostatic repulsion. Hydrophilic colloids which are ionogenic at least owe part of their electrokinetic p.d. to ionization at fixed points on the particle surface. All of these points obviously can not be in contact. It is probable therefore that there is some residual electrostatic repulsion even between particles coherent over a part of their surfaces.

(3) The tendency of the water molecules to wet hydrophilic substances in the surfaces of the coherent particles may tend to force these coherent surfaces apart.

It is also possible that statistical fluctuations in the internal energy of the molecules of colloidal particles in contact must be taken into account in a complete treatment of dispersive forces. (In this general connection see Burk: J. Phys. Chem., 35, 2446 (1931).

the energy provided by the dispersive forces the particles will cohere after contact. If it is less the particles will separate again after collision. Obviously here too, as in the case of the repulsive force, there must be a value of Wc which will just balance the dispersing tendency in any case. This may be called the critical value of Wc.

As in the case of the concept of a critical repelling force, so also in the case of the concept of a critical work of cohesion, it is important to bear in mind the statistical distribution of kinetic energies. The Brownian motion impulses tending to separate particles in contact vary in magnitude in a statistical manner. The critical work of cohesion for a system of dispersed particles is therefore such that a sufficient majority of the impulses tending to separate particles in contact fail to do so.

It is apparent from the foregoing considerations that if the repelling force is greater than its critical value, a dispersion will be stable. The same is true if the work of cohesion is less than its critical value.

The question of the variation of the work of cohesion merits particular discussion at this point, remembering that the present discussion applies to dispersions in aqueous media. The work of cohesion has been defined as equal to $2\ S\gamma AB$. The variation of work of cohesion from case to case is therefore primarily a matter of variation in the free surface energy at the respective particle-dispersion medium interfaces. In general, in accord with Harkins,[45] the more nearly similar the dispersion medium and the surface material of the particles, the lower the expected interfacial tension. In this connection, it is most important that certain colloidal particles have the property of associating themselves with large quantities of water from their dispersion medium.[46] It is not necessary at this point to discuss the possible mechanisms involved[47] in the taking up of the water. It is highly probable that different mechanisms are operative in different cases.[48] It is however also highly probable that in some of these cases the combination of the particles with water results in a hydrous particle surface, which is much more similar to water in the Harkins sense than the surface of a particle of the same substance in the anhydrous condition. In such cases the interfacial tension of the particles against their dispersion mediums is presumably lowered and along with it the work of cohesion of the particles. It would seem that the lowering of work of cohesion due to the hydration of the surface of dispersed particles must be considered as a potential factor affecting the work of cohesion between them and thus the stability of dispersions of such particles in aqueous media.

The relationship of the foregoing material to the well known experimental facts with regard to the stability of colloidal solutions is fairly obvious. Colloidal particles dispersed in aqueous media, may be conveniently considered in two classes for purposes of discussion, as hydrophobic particles and hydrophilic particles.[49] The first class have little or no affinity for water and the second a marked affinity.

In the case of dispersions of hydrophobic particles clear-cut experimental evidence[50] has shown that the necessary condition for their stability is that the electrokinetic potential difference at the surface of the particles exceed a

certain limiting value known as the critical potential.[51] When the electrokinetic potential falls below this value aggregation of the particles takes place. The electrokinetic potential difference between particles and their dispersion medium results from the existence of an electrical double layer at the surface of the particles. The particles are positively or negatively charged with respect to the medium depending, respectively, upon whether the positive or negative side of the electrical double layers is associated with the particles.[52] It is believed that the repelling action of similarly charged particles is responsible for the stability of suspensions of hydrophobic particles when the electro-kinetic potential exceeds the critical value.[53]

In terms of the general working theory of suspension stability which has been presented, this type of electrostatic repulsion is the repelling force which if sufficient can prevent the contact of particles when opportunity for their collision is provided in virtue of their Brownian motion, and thus stabilize the dispersion. So far as is known, there is no other type of repelling force to be considered. The critical potential in the case of a single collision may now be defined as that electrokinetic potential difference which is just sufficient to prevent the contact of two particles when Brownian motion offers the opportunity for their collision. The concept of the critical value of a repelling force for a system of dispersed particles has been discussed.

Turning now to the question of the stability of hydrophilic colloidal particles, it is found that quite a different situation prevails. Kruyt and others working in his laboratory[54] have clearly demonstrated that the condition of hydration of certain hydrophilic colloidal particles must be considered as a stabilizing factor in dispersions of such particles in aqueous media. The first outstanding fact is that certain of the particles studied formed stable dispersions when their repelling force, as measured by their electrokinetic potential, was reduced to zero.[55] The addition of sufficient alcohol to such isoelectric dispersions caused them to precipitate. The alcohol in such cases is generally considered to act by dehydrating the particles. These facts indicate first that a stabilizing factor is active apart from electrokinetic potential difference, and secondly that this stabilizing factor results from the hydrated condition of the particles. It is apparent that this second stability factor is capable of stabilizing a dispersion of these particles in complete absence of a repelling force. It must therefore act by decreasing the work of cohesion of the particles below the critical value or by raising this critical value. Reasons for this stabilizing action associated with the hydrous condition of the particles then follow directly from the previous discussion. It was pointed out that increased surface hydration should accompany the union of hydrophilic particles with water of the dispersion medium. This increased surface hydration should cause the hydrated particles to have a much lower surface tension against the aqueous dispersion medium than would the same particles in a hypothetically anhydrous condition. Certain hydrous particles might well thus have very low surface tensions against aqueous media which in turn would cause them to have very low works of cohesion, even possibly below the critical value. In this way the hydrous condition of particles in

certain cases could be a stability factor which could result in the stability of a suspension of such particles even when their electrokinetic potential was reduced to zero. Moreover the tendency of the water to wet the hydrophilic surfaces might promote dispersion and therefore necessitate a high critical value of the work of cohesion.

The mechanism outlined above is here offered as the one which is operative in the unquestioned stabilizing influence of the hydrous condition of the particles in hydrophilic suspensions. It is significant that the only dispersions of colloidal particles in aqueous media which are known to be stable in the absence of electrokinetic potential are those in which independent evidence points clearly to the hydrophilic nature of the particles.

It should be pointed out that the concept of variation in the work of cohesion with surface hydration applies to variation in the state of hydration of a particular surface. In passing from one surface to another, as in the deposition of a protective or sensitizing film, no such relationship necessarily exists. Surface A may be less hydrous than surface B and still have a lower work of cohesion. The point is that surface A for example presumably has a lower work of cohesion in a relatively hydrated state than in a relatively dehydrated state. In the sense of this paper, changes in hydration of a particular surface such as may be brought about by the electrolyte content of the medium are considered as modifications of an existing surface rather than the formation of a new surface.

The critical potential as experimentally determined for a system of dispersed particles is the minimum electrokinetic potential compatible with a stable condition of the dispersion under the defining conditions. Suppose that the work of cohesion is sufficiently high so that practically every contact results in permanent coherence of particles. The experimentally determined critical potential will then be such that it is just sufficient to prevent a sufficient majority of contacts when opportunity for collision is offered due to Brownian motion. If the work of cohesion is somewhat lower, that is if an appreciable number of contacts result in redispersion, the repelling force would not have to be quite so large, that is it would not have to prevent as many contacts as before in order to maintain stability. In this second case, the experimentally observed critical potential would be somewhat lower than in the first.

Theoretically therefore, experimentally determined critical potentials should decrease with decrease in work of cohesion in all cases where the work of cohesion is less than sufficient to prevent practically all redispersion. When the work of cohesion is sufficiently small the suspension will be stable even at zero electrokinetic potential. In this connection it is interesting that March, using several assumptions, has calculated that the charge corresponding to the critical potential observed by Powis for stable, pure oil-in-water dispersions is not sufficient alone to account for the stability of the system. The indication therefore is that the work of cohesion of the oil droplets is lowered in consequence of the existence of some form of hydrous interfacial film. (See March: Koll.-Z., **45**, 97 (1928); Heymann: Koll.-Z., **48**, 195 (1929).

Shibley[56] confirmed the critical potential value of Northrop and De Kruif ($\pm$ 15 millivolts) with bacteria suspended in NaCl, ZnSO$_4$ and CeCl$_4$. In the presence of Na$_2$HPO$_4$, however, the same microorganisms had a much higher critical potential (-34.6 millivolts in one experiment). It is possible that the higher critical potential in the presence of Na$_2$HPO$_4$ was due to an increase in work of cohesion due to this particular salt.

Aggregation occurs when the electrokinetic potential difference is lower than its critical value in any system of dispersed particles, whose cohesive force is above its critical value. However the *rate* of aggregation within the critical potential zone varies with the residual charge upon the particles, being most rapid at the isoelectric point.[57] One reason is that the lower the charge the greater the majority of total opportunities for collision which result in contact, with all opportunities for collision resulting in contact at the isoelectric point. Further, it has been suggested that residual charge is a factor aiding the redispersion of particles after contact, at least in some cases. In these cases, the greater the residual charge, the greater the redispersion tendency and presumably the slower the rate of aggregation.

The relationship of stabilizing and sensitizing surface films to the general question of the stability of dispersions of colloidal particles in aqueous media is secondary to the factors which have been discussed. It will be treated in the section of the paper dealing with the stability of suspensions of sensitized bacteria.

As has been mentioned earlier in the paper, Reiner, in connection with his excellent experimental work on the analogous behaviour of bacteria which have been treated with antisera and tannin solutions, has offered a general treatment of the stability of suspensions of particles in water.[32] It was further stated that the present writers believe this theoretical treatment to be in error. Reiner's fundamental thought is that the conflicting forces in determining the stability or non-stability of a dispersion are cohesion, acting to cause aggregation of the particles, and adhesion, acting between the aqueous medium and the particles, tending to keep the particles dispersed.

He states that the work of separation incident upon increased dispersion of a microheterogeneous system is given by the expression

$$\tfrac{1}{2} \, ds(2\gamma A + 2\gamma B) *$$

where ds is the increase of surface of the disperse phase, and γA and γB are respectively the "free surface energies" of the dispersed material and the dispersing medium. This formulation is incorrect. As has been pointed out the work of cohesion is given by the expression,

$$Wc = 2S\gamma AB$$

where γAB is the free surface energy at the particle-dispersion medium interface. γA and γB do not enter the expression, because the only free surface energy changes in the aggregation and dispersion of particles immersed in an aqueous medium are respectively decreases and increases in the extent of the

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* Reiner's actual expression is translated into the notation of this paper.

particle-dispersion medium interface. Therefore the only free surface energy involved is the corresponding free surface energy, namely γAB.

Reiner goes on to define the affinity of the particles for water as measured by the work of adhesion in terms of the Dupré equation,

$$W_A = \gamma A + \gamma B - \gamma AB,$$

where W_A is the work of adhesion and the other symbols have the same significance as in the previous equations. Without going into detail it may be said that the Dupré equation is not applicable to the aggregation and dispersion of particles of a single substance immersed in an aqueous medium. γA and γB do not enter the situation at all for the reasons indicated in the discussion of Reiner's equation for cohesion.

Reiner then says that the tendency for the aggregation of particles, or "attraction," is measured by the difference between the cohesion and adhesion, and that this is equal for unit area to the particle-aqueous solution interfacial free energy. Since the premises are not correct it would seem that there were no need for considering the conclusion further. It may be pointed out, however, that Harkins, Clark and Roberts[58] have measured the works of cohesion and adhesion for a large number of substances and the differences between the two by no means equal the free interfacial energies of the interface between the adhering substances. Reiner's result happens to be equal to the work of cohesion tending to hold particles together after they have made contact. The relation of the work of cohesion to the stability of dispersions of colloidal particles has been discussed at length in the present paper.

The Stability of Suspensions of Unsensitized Bacteria

The work of Northrop and De Kruif[24,25] has been of great importance in the development of the theory of bacterial agglutination. The stability of the suspensions of the two types of bacteria which they studied varied markedly and regularly with the salt content of the dispersion medium. With salt concentrations below 0.001 molal both types regularly agglutinated when their electrokinetic potential was reduced below ± 15 millivolts. Under these conditions ± 15 millivolts was the critical potential. When the total salt concentration was raised to 0.1 molal, the suspensions were stable when the electrokinetic potential was reduced to much smaller values than ± 15 millivolts, in some cases even when it was reduced to zero.

Shortly after the work of Northrop and De Kruif, Loeb[59] showed that the stability of gelatin solutions is influenced by salts in an exactly similar way, and further that the stability of suspensions of collodion particles coated with surface films of gelatin also showed the same type of behaviour. Loeb[60] pointed out the similarity of his results of this type to those obtained by Northrop and De Kruif with bacteria. He concluded from his experimental work that the increased stability of the suspensions of protein-coated collodion particles in the higher salt concentrations was most probably due to increased affinity of their surfaces for water under these conditions. Later Oliver and Barnard[61] and Netter[62] also attributed the decrease in "cohesive force" of the surface

of cells by salts to increased affinity of the surfaces for water. It would seem highly probable on this basis that the increased stability of the bacterial suspensions of Northrop and De Kruif may also have been due to an increase in the hydrous condition of the surfaces of the bacteria in the higher salt concentrations. This probability also follows from the theoretical considerations which have been presented in this paper.

Since the suspensions were stable in some cases even when the electrokinetic potential was reduced to zero, it follows that the work of cohesion of the bacteria must have been reduced below its critical value. It was shown that the most probable cause for the reduction of the work of cohesion between particles dispersed in aqueous media, is an increase in the hydrous condition of the particle surfaces. Changes in salt concentration are well known to affect the state of hydration of hydrophilic colloidal particles, and hence very probably to alter their state of surface hydration.

Northrop and De Kruif clearly recognized that a decrease in "cohesive force" must have taken place as between their bacteria in 0.001 and 0.1 salt solution. As has been described in the first part of this paper, they devised and used an ingenious method for following changes in this value. They defined "cohesive force" by the values obtained by this method. There is some question as to whether the values obtained by them accurately expressed the value of the cohesive force as defined in this paper, because, for example, their method may well have involved work against viscosity in the separation of partially coalescent particles. Nevertheless, in any case, they definitely showed that a reduction in "cohesive force" as measured by their method always accompanied the phenomenon of suspension stability with electrokinetic potentials below ± 15 millivolts. This parallelism is convincing evidence that they were able to measure true cohesive force with sufficient accuracy to arrange their suspensions in the proper order with regard to their value, and that was the most important object of their "cohesive force" measurements.

It is apparent that the foregoing discussion does not add greatly to the conceptions of Northrop and De Kruif. Their work preceded the work of Kruyt's laboratory on the stabilizing action of hydration. Because of the more recent emphasis placed upon the hydration factors, it seems of value to indicate the relation of this factor to the results of Northrop and De Kruif. Briefly, we believe the hydration to be one of the factors which determines the "cohesive force" of Northrop and De Kruif and the critical value of the cohesive force.

Northrop and De Kruif further showed that if the salt concentration is increased well beyond 0.1 molal their bacterial suspensions again became unstable. There seems to be no question but that they were correct in attributing this to a "salting out" mechanism, that is to a dehydration and precipitation in the presence of a high salt concentration. The general conclusion from their results is that both electrokinetic potential difference and hydration are important factors in determining the stability of suspensions of the two types of bacteria studied by them, both being markedly affected by variations in the total salt content of the dispersing medium.

According to Northrop and De Kruif, the lowest concentrations of salts acted to affect the electrokinetic potential difference, medium concentrations to affect the "cohesive force" and still higher concentrations to affect the state of surface hydration. In the opinion of the present writers, it appears that the effect of the intermediate concentrations on "cohesive force" may also be interpreted as resulting from an effect on the hydration affinity of the bacterial surfaces.

The general indicated dependence of the stability of Northrop and De Kruif's bacterial suspensions upon both electrokinetic potential difference and hydration, clearly indicates that the surfaces of their bacteria resemble hydrophilic colloids. The similarity of behaviour shown by Loeb's collodion particles with gelatin surfaces is confirmatory evidence for this view.

Bacteria do not all have surfaces of this type, however. The interfacial technique of Mudd and Mudd[9,10] has enabled them to study the relative ease of wetting by oil and water of the surfaces of a large number of different types of bacteria. They have found in this way that acid-fast bacteria are in general more readily wet by oil than by water, whereas non-acid-fast bacteria in general are much more readily wet by water. It would be expected on this basis that stability relations of suspensions of acid-fast bacteria would resemble those for hydrophobic colloidal particles rather than those for hydrophilic particles as found in the case of Northrop and De Kruif's bacteria.

Further we have cultures of three types of bacteria which have the exceptional property of forming stable dispersions in distilled water or acid less than 0.001 molal with electrokinetic potentials of the order of 0 to a few millivolts, i.e. well below the critical value of ± 15 millivolts operative in the case of the two types studied by Northrop and De Kruif, when the electrolyte content of the dispersion medium was less than 0.001 molal.

The general contention of Northrop and De Kruif was that the stability of their bacteria with very low electrokinetic potentials when the salt content was increased to above 0.1 molal, was that the increased concentration depressed the cohesive force of the bacteria. Since the above-mentioned three types of bacteria form suspensions which are stable in distilled water or very dilute acid, with electrokinetic potentials of 0 to a few millivolts, it is apparent that an extension of the views of Northrop and De Kruif is necessary to account for the stability of these suspensions.

According to the theoretical conclusions of the present paper it appears necessary that this type of stability is due to an extremely low work of cohesion due to surface hydration which is probably in excess of that obtaining in the case of the bacteria of Northrop and De Kruif. It is at least quite definite that the primary stabilizing action of hydration is operative over a wider range of conditions in the case of the three varieties described here. Acid-fast bacteria and the type just described represent extreme types selected from a large number of bacteria studied over a period of years on the basis of their wetting properties and cataphoretic behaviour. The two types seemed to offer splendid material for the extension of the general theory of the stability of bacterial suspensions.

Accordingly experiments have been performed to test the hypothesis that the stability of suspensions of acid-fast bacteria depend upon conditions more closely resembling those for the stability of dispersions of hydrophobic colloidal particles; and that the varieties with apparently markedly hydrous surfaces form suspensions whose stability depends more definitely upon the hydration factor, than do those of the suspensions of the two types of bacteria studied by Northrop and De Kruif.
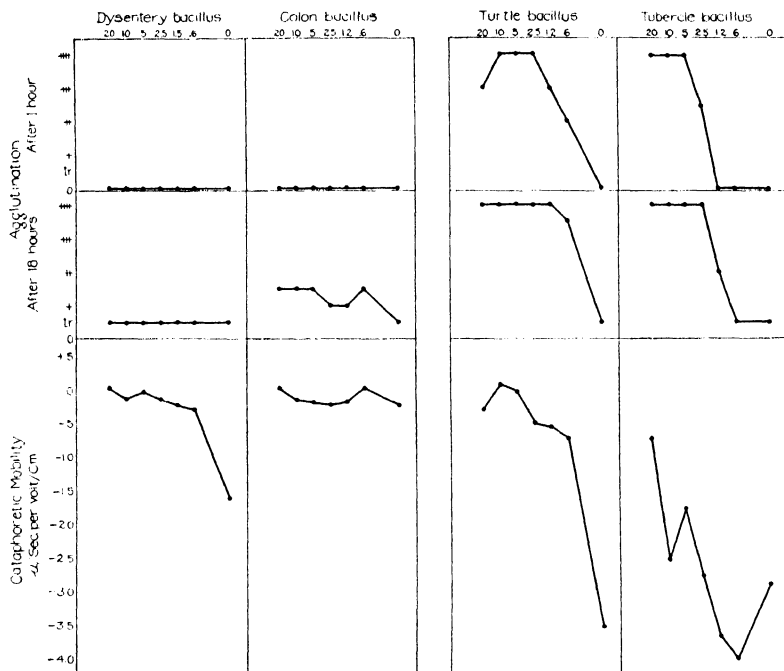
FIG. 2

Stability of hydrophilic bacilli and precipitation of hydrophobic bacilli in presence of acid. Washed bacteria suspended in solutions of HCl in distilled water. Abscissae, concentrations of HCl in millimols per liter. The hydrophilic dysentery and colon bacilli show little aggregation at any acidity. The hydrophobic turtle and avian tubercle bacilli show complete aggregation in acid concentrations which sufficiently reduce the electrokinetic p.d. To obtain electrokinetic p.d. in millivolts in this and subsequent figures multiply μ/sec. per volt/cm. by 12.6. (In this connection see Northrop and Cullen: J. Gen. Physiol., 4, 638 (1921-22).

Fig. 2 records such an experiment. Washed suspensions in distilled water of two of the hydrophilic bacteria, the dysentery and the colon bacillus, and two acid-fast hydrophobic bacteria, the turtle bacillus and the Arloing strain of avian tubercle bacillus, were mixed with water and with dilute HCl solutions. The concentrations of HCl after mixing, in millimols per liter, are given as abscissae. Agglutination was read after one hour and after 18 hours in the ice box. The cataphoretic mobilities were determined in a microcataphoresis cell[12] following the 18 hours reading. Each suspension was examined in the cataphoresis cell in HCl of the same concentration as that in which the agglutination readings had been made.

It is apparent that only a trace of agglutination of the dysentery bacillus occurred in any acid concentration, although the electrokinetic p.d. was extremely low; in 0.6 millimolar HCl the p.d. for the dysentery bacillus was about 3 millivolts. The colon bacillus showed very little agglutination although the p.d. was minimal; the colon bacillus was stable in distilled water with a p.d. of only about 3 millivolts. It is obvious that the stability of the colon bacillus in distilled water is neither attributable to reduction of the cohesive force by electrolytes nor to a high surface charge.

Mols of Na Cl per liter
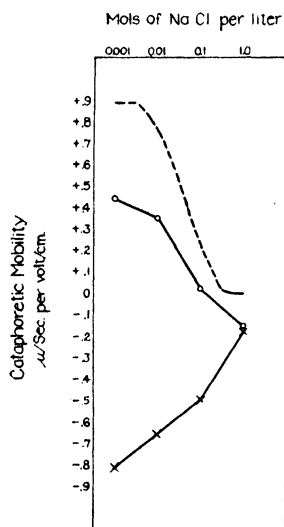
FIG. 3

Effect of salts on p.d. and lack of effect on agglutination of turtle bacillus and avian tubercle bacillus. Bacteria were suspended in 0.01 N HCl to which were added the amounts of NaCl indicated on the axis of abscissae. Circles, turtle bacillus. Crosses, avian tubercle bacillus. The upper broken line is the curve for typhoid bacillus in HCl and NaCl, redrawn from Northrop and De Kruif's[24] Fig. 4, p. 647. Unbroken line, complete agglutination. Broken line, no agglutination. The high electrolyte content inhibits agglutination of the typhoid bacillus, but not that of the hydrophobic acid-fast bacteria.

The turtle and avian tubercle bacillus, on the other hand, which in an oil-water interface show marked preferential wetting by the oil,[9] are rapidly aggregated in concentrations of acid sufficient to reduce the p.d. below its critical value. In the case of the avian tubercle bacillus the value of this critical potential seems to be high, nearer that found by Powis[63] for oil drops than that found by Northrop and De Kruif for non-acid fast bacteria.

In Fig. 3 the same two acid-fast bacteria are set up in strongly acid solutions containing graduated concentrations of NaCl. The concentration of HCl after mixing was N/100 in each tube. The NaCl contents in the several tubes were 0.001, 0.01, 0.10 and 1.0 molar, respectively. These experimental conditions were chosen to duplicate as nearly as possible those of Fig. 4 in the paper of Northrop and De Kruif.[24] In our experiment the acid reduced the potential below the critical value for the hydrophobic bacteria and agglutination occurred in all tubes in spite of the very high electrolyte concentration. The corresponding curve in Northrop and De Kruif's Fig. 4 is replotted for contrast. With these bacteria no agglutination occurred until the very high "salting out" concentration was reached.

The general conclusions of this section of the paper may now be stated. Bacteria exist which display a wide range of surface types, from those which are markedly hydrophobic to those which are markedly hydrophilic. The factors governing the stability of dispersions of the various types in aqueous media are the same as apply to the stability of colloidal particles with similar types of surfaces. The theoretical considerations are those which have been described in a previous section.

Bacteria with strongly hydrophobic surfaces are stabilized in aqueous media chiefly by electrokinetic potential difference. They agglutinate when their electrokinetic potential is reduced below a definite relatively high critical value. Others, of the type studied by Northrop and De Kruif, form suspensions in which both electrokinetic potential difference and hydration are stabilizing factors of primary importance. This is not difficult to understand since evidence has recently been brought forward to indicate that the surfaces of many or most bacteria contain both hydrophobic and hydrophilic components.[64] Finally bacteria exist whose state of surface hydration is the primary stabilizing factor in their dispersions in aqueous media over a wide range of conditions.

The Stability of Suspensions of Sensitized Bacteria

"Sensitized" bacteria are bacteria which have combined with their corresponding antibodies. Sensitization results in marked changes in the physical properties of the bacterial surfaces, i.e. the sensitized bacteria are more cohesive, their wetting properties are altered, their electrokinetic p.d. is, under the conditions of the usual serological experiment, reduced, and their isoelectric point is shifted to a value near (but often not identical with) that of serum globulin.[3,16] As was pointed out earlier in this paper these changes are consequent upon the formation of a surface deposit of antibody-globulin on the antigen. Since electrokinetic p.d., cohesion (and hydration), are the fundamental factors determining stability, the stability of sensitized would be expected to differ from that of unsensitized bacteria. As a matter of fact agglutination is the most familiar consequence of combination with antibody.

The remarkable specific chemical affinity between antigen and antibody enables the antibody in exceedingly high dilution to form an effective surface deposit on the antigen. Thus antisera may be prepared which agglutinate typhoid bacilli in a dilution of one volume of serum in a hundred thousand volumes of diluent. The surface deposit once formed, however, has many points of resemblance to deposits of serum proteins, egg albumin or other proteins formed by non-specific adsorption on bacteria or other particles. The non-specific deposit of serum proteins, in addition to requiring much higher concentration of protein to form an equivalent deposit, is in general less firmly held than the specific deposit.

In general with the progressive formation of a surface deposit the electrokinetic p.d. and isoelectric point of the particle approach those of the deposited substance. The stability conditions in the case of gelatin adsorbed on collodion particles have been shown by Loeb closely to resemble these of gelatin solutions.[65] Loeb showed on the other hand that collodion particles coated with egg albumin showed the stability relations of denatured albumin rather than those of native albumin.[66] As was pointed out in the first section of this paper, students of specific bacterial agglutination from Bordet on have been impressed with the fact that sensitized bacteria were aggregated by traces of cations which were alike incapable of precipitating the unsensitized (non-acid fast) bacteria or the serum globulins with which the antibodies are associated.

The antibody-globulin combined with antigen has therefore been spoken of by Shibley[13] and others as "denatured."

Northrop has discussed the general question of the change in the stability relations of suspensions of particles when their surfaces become coated with any variety of surface film. His discussion is on the basis of changes in electrokinetic potential difference and the changes in the "cohesive force."[15] This same question may be discussed advantageously from the point of view of suspension stability presented in the present paper in a manner in which the general conceptions are very similar to those of Northrop.

A given dispersion of particles is stable either if the repelling force (electrokinetic potential difference) is greater than its critical value, or if the cohesive force of the particles ($2S\gamma AB$) is below its critical value. It follows from this that for aggregation and precipitation to occur both the electrokinetic potential difference must be below its critical value and the work of cohesion must be above its critical value.

A stabilizing or protective film forming substance is one that, under the conditions of test, results in a surface such that either the electrokinetic potential difference is above the critical value for that surface or that the work of cohesion of the surface is below its critical value, or both. A precipitating or sensitizing film forming substance is one such, that under the conditions of test, a surface results which is both below its critical potential and above its critical work of cohesion. It is apparent that one and the same substance may act either as a stabilizing or sensitizing film forming substance depending upon the conditions of test.

Since after combination with bacteria has occurred, the effect of antibody film on stability conditions is entirely analogous to that of other types of films, the above considerations apply to the agglutination of sensitized bacteria. It may immediately be stated that antibody films which cause agglutination of bacteria do so because they result in surfaces which are both below their critical potentials and above their critical works of cohesion under the conditions of test. It is misleading to state that the agglutination of bacteria by antibodies results "from a decrease in electrokinetic potential difference" or "from an increase in cohesive force."

Reiner's view that the sensitized surfaces are always less hydrous than the corresponding unsensitized bacteria, and that this difference in hydration is the fundamental change responsible for the agglutination of sensitized bacteria is obviously incomplete on the above basis. In this connection it will be remembered that it has been pointed out that dehydration of a given surface would be expected to lead to an increase in cohesive force. However, since in depositing an antibody film, we are forming an entirely new surface, this general relationship need not necessarily hold.

The conclusion of Tulloch[19] and others that sensitized bacteria behave relatively more like denatured protein surfaces and that many unsensitized bacterial surfaces behave relatively more like normal protein surfaces, and Northrop and De Kruif's[24,25] observations on the variation with the salt content of the medium of the cohesive force of these sensitized and unsensitized

suspensions both support the view that the sensitization of non-acid fast bacteria does give them surfaces which are less hydrated than in the unsensitized state.

However, several classes of carefully studied cells in the unsensitized condition show in an oil-water interface marked preferential wetting by the oil. After specific serum sensitization these same cells show marked preferential wetting by the aqueous phase of the interfacial preparations. Many acid-fast bacteria, notably the turtle and avian tubercle bacilli,[14] red blood cells[67] and certain spirochetes[68] belong in this category. Sensitization in brief has been found by direct observation greatly to increase the difficulty with which water may be displaced by oil from the surfaces of cells of this class. It is reasonable to conclude that sensitization of these relatively hydrophobic cells has increased, rather than decreased, their surface hydration.

Yet sensitization of the hydrophobic cells of this class produces an increase in cohesiveness only slightly less striking than in the case of hydrophilic bacteria. This increase in cohesiveness may be directly observed in gross by the resuspension technique and microscopically by the interfacial technique. These instances afford clear examples of the fact that formation of a new surface as in sensitization, may result in increased cohesion, accompanied either by an increase or decrease in hydration, or at least in relative ease of wetting by water as compared to oil.

The interesting imitation by tannin of several manifestations of antibody action, first demonstrated by Reiner and his associates, makes it desirable to learn more about the effect of tannin on surfaces treated with it. We have studied the adsorption of tannin on a variety of substances. Mixtures of the test bacterial or other suspension were made with serial dilutions of tannin, the precipitates were washed and their cataphoretic mobility was determined in a microcataphoresis cell. It has thus been found that tannin forms an electronegative surface deposit, whose cohesion and precipitability by salts is somewhat greater than those of the untreated bacteria.

The detailed procedure was usually as follows:

A 10% solution of tannic acid (Merck's "Reagent") in distilled water was made. To one volume of this 10% solution an equal volume of 0.1 N NaOH was added. The pH of this mixture was usually from 6.0 to 6.7. Serial dilutions of this stock 5% neutralized tannin solution were made in 0.85% NaCl; dilution was usually in powers of 4, 1:4, 1:16, 1:64, etc. Equal volumes of the test suspension in 0.85% NaCl solution were added to the serial tannin dilutions. The series were kept overnight in the icebox and *agglutination* was read in the morning. All tubes were centrifuged and the supernatant fluids were decanted. A few drops of 0.85% NaCl solution were added to the sediment in each tube and these were shaken uniformly in a rack until the sediment in the control tubes was evenly suspended. The degree of aggregation of the treated sediments was recorded. These results are plotted as *resuspension*. Excess 0.85% NaCl was added to each tube and these were again centrifuged and the supernatant fluids decanted. The washed sediments were shaken up in 0.85% NaCl and studied in appropriate buffers in the microcataphoresis cell. In series in which serial dilutions of serum were used instead of tannin the subsequent procedure was the same.

The result of such an experiment is shown in Fig. 4. The test suspension in this case was a "rough" pneumococcus which was isoelectric at about pH 4.3. The bacteria were agglutinated and made more cohesive both by horse

immune serum and by tannin. The isoelectric point of the treated and washed bacteria was, however, shifted by the immune serum to a value of about pH 5.55, and by tannin the isoelectric point was shifted progressively toward the acid side to a pH below 1.8.

Another experiment is shown in Fig. 5. In this case a dysentery bacillus (Flexner type) was agglutinated by the serum of the patient from whom it was isolated and by tannin. This micro-organism had no measurable p.d. in M/50 acetate buffer of pH 4.4. Sensitization with the patient's serum gave these bacteria an electrokinetic p.d. with isoelectric point at pH 5.4. Treatment with progressive concentrations of tannin gave the bacteria suspended in acetate of pH 4.4 an increasing negative p.d.

"Smooth" pneumococci, with their carbohydrate-rich capsules, were also
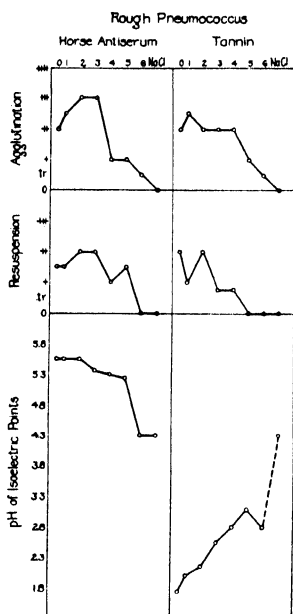
FIG. 4

The effects of specific immune serum and of tannin on the agglutination, resuspension (cohesiveness) and isoelectric point of a rough pneumococcus, isoelectric at pH 4.3. Bacilli treated with serum or tannin, washed, and studied in microcataphoresis cell. Abscissae dilutions, in powers of 4, of serum or of stock 5% neutralized tannin solution. i.e. 1 indicates four times diluted; 2 indicates 16 times diluted etc. In these experiments and in those illustrated in subsequent figures, all mixtures of bacterial suspensions with serum or tannin solutions contained equal volumes of the suspension and of the solution.
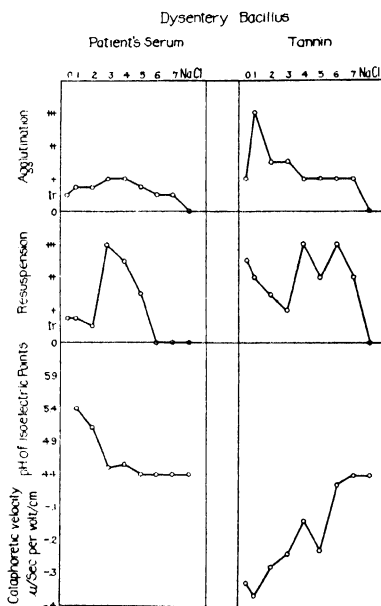
FIG. 5

The effects of specific immune serum and of tannin on the agglutination, resuspension (cohesiveness) and isoelectric point of a hydrophilic bacillus. Abscissae as in Fig. 4. The unsensitized bacillus was practically uncharged in buffer of any pH used. After sensitization with serum charge and isoelectric point near pH 5.4 were acquired. After treatment with tannin a negative charge was acquired.

agglutinated by tannin. Since these bacteria were electronegative even in acid solutions, however, little change in the electrokinetic p.d. as a result of adsorption of tannin was demonstrable.

The turtle bacillus proved very sensitive to agglutination by tannin. Suspensions of these bacilli were agglutinated by as little as 1 part in 100,000 of tannic acid or neutralized tannin. It would be difficult to suppose that agglutination of this hydrophobic bacillus was due to "dehydration."

With one exception all types of bacteria and other particles aggregated by strong tannin solutions were electronegative even in acid solutions. The exception was red blood cells which after treatment with strong tannin solutions developed isoelectric points in the neighborhood of pH 6.0. This result was very puzzling until it was observed that collodion particles added to these tannin-treated red blood cells promptly became isoelectric at about the same pH as the treated red blood cells. Collodion particles treated with tannin alone are strongly electronegative. It was thus evident that treatment with strong tannin solutions injured the red blood cells with liberation of some amphoteric substance which was readily adsorbed on the surfaces of the red cells themselves and of collodion particles. A similar source of error has been described by Abramson[69] for red blood cells in acid buffers and by Mudd and Mudd for white blood cells in acid buffers.[70]

The resuspension observations plotted in Figs. 4 and 5 and also those plotted later in Fig. 6 and Fig. 7 refer to the relative ease with which the bacteria may be resuspended by mechanical agitation, after agglutination has proceeded for 18 hours and all suspensions have been centrifugalized. The difficulty of resuspension varies over wide limits, and while it frequently parallels the degree of agglutination, it may be partially independent of this value. Thus turtle bacilli are completely agglutinated both by their specific antiserum and by appropriate concentrations of acid. In the former case, they may be resuspended only with difficulty. In the latter resuspension is accomplished by very slight mechanical agitation.[71] The fact that complete agglutination occurs in both cases, means that the work of cohesion exceeds the critical value in both cases. In the ideal case the resuspension test then furnishes a rough measure of the *extent to which the work of cohesion exceeds the critical value.* However in cases such as that of the agglutination of bacilli with specific antiserum it is probable that coalescence of surface antibody-films occurs on standing and centrifugalization after primary agglutination. The separation of coalesced particles is non-ideal and involves work against viscosity. The resuspension test thus measures composite differences in ideal work of cohesion combined with any differences which may exist due to different degrees of coalescence of different surfaces. In Figs. 4, 5, 6 and 7, the difficulty of redispersion parallels the degree of agglutination in all cases.

Since most bacteria are strongly electronegative at reactions approaching neutrality the usual result of serum sensitization is a reduction of electrokinetic p.d. The charge of the partially sensitized bacteria is a resultant of that of the bacteria themselves and that of the antibody-protein deposited

on the surface.   The availability of three strains with negligibly small intrinsic surface charge offered the opportunity therefore to study the changes incident upon sensitization under somewhat simplified conditions.

In the experiments recorded in Figs. 6 and 7 the colon bacillus, dysentery bacillus and S. pullorum are sensitized each with a corresponding rabbit immune serum.   In the experiment shown in the first column of each figure the bacteria were washed and suspended in M/14 acetate buffer of pH 4.4.   The second columns show data with the bacteria washed and suspended in M/15 phosphate buffer of pH 7.3.   In each case 1 cc. of bacterial suspension was mixed with an equal volume of each serial dilution of immune serum.   The mixtures were incubated 2 hours at 37° and left overnight in the ice box.   The agglutination was read in the morning; all tubes were centrifugalized, the supernatant fluids were decanted and a few drops of buffer were added to each tube.   The tubes were shaken together in a rack and the results recorded as "resuspension."   More buffer was then added, all
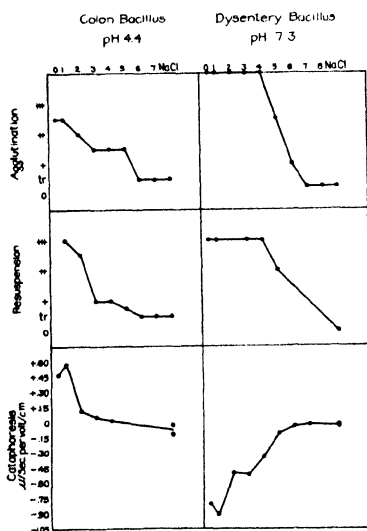
FIG. 6

The effects on agglutination, resuspension (cohesiveness) and electrokinetic p.d. of specific serum sensitization of hydrophilic bacteria.   In the first column a strain of colon bacillus, suspended in M/14 acetate buffer of pH 4.4, is sensitized with rabbit immune serum.   In the second column a dysentery bacillus (Flexner strain) suspended in M/15 phosphate buffer of pH 7.3, is sensitized with rabbit immune serum.   Bacilli washed after sensitization and suspended in the corresponding buffers.   Ordinates, intensities of reaction.   Combination of antibody with antigen occurs on both sides of isoelectric point of antibody. Agglutination occurs parallel to increasing cohesiveness in spite of increasing charge, which may be either positive or negative.
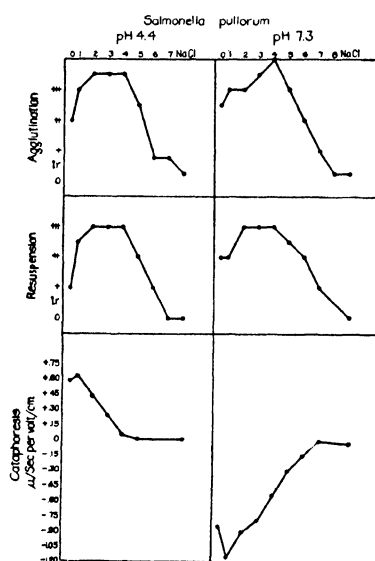
FIG. 7

The effects on agglutination, resuspension (cohesiveness) and electrokinetic p.d. of specific serum sensitization of hydrophilic bacteria.   In the first column a strain of Salmonella pullorum, suspended in M/14 acetate buffer of pH 4.4, is sensitized with rabbit immune serum.   In the second column the same bacillus, suspended in M/15 phosphate buffer of pH 7.3, is sensitized with rabbit immune serum. Experimental procedure and coordinates as in Fig. 6.   Combination of antibody with antigen occurs on both sides of isoelectric point of antibody. Agglutination runs parallel to cohesiveness in spite of increasing charge. Note "agglutination prezone."

tubes were again centrifugalized, the supernatant fluids were decanted and the washed sediments were again shaken up in buffer. Microcataphoresis determinations were finally performed. Similar buffer mixtures to those used in making the original suspensions were of course used throughout the washing and cataphoresis determinations.

Figs. 6 and 7 show that antibody combines on both sides of its isoelectric point with antigen; this fact was already well known.[72,73,74] They show, that in these cases agglutination was correlated with actual increases of electrokinetic p.d., the sign of charge being positive in the acid and negative in the acid buffer. Since the electrokinetic p.d.s throughout the whole experiment were within the critical potential zone for sensitized cells, this unusual correlation of decreased stability with increased charge is readily understandable. The decreased stability in these cases is evidently due to the substitution of cohesive, little hydrated antibody-protein surfaces for the strongly hydrated bacterial surfaces.

Attention is finally directed to the submaximal agglutination which occurred with the highest concentration of sensitizing serum in Fig. 7. This is the so-called "agglutination prezone" which is familiar to immunologists. A detailed discussion of this phenomenon would be outside the scope of this paper. It is worth pointing out, however, that this is not, as is sometimes supposed in uncritical treatments of the subject, due to the same mechanism as the zone phenomena observed in the mutual precipitation of positively and negatively charged colloids. For a critical study of the agglutination prezone the reader is referred to Shibley.[75]

Summary

The first portion of the paper is devoted to an historical summary of the development of the present state of knowledge of bacterial agglutination.

A theoretical formulation of the factors affecting the stability of dispersions of colloidal particles in water and aqueous media is next presented. The treatment is not exhaustive, but rather aims to present a general statement of the modes of action and the interrelationships of the major physical factors governing stability, i.e. charge, cohesiveness (which can be expressed in terms of surface energy), and hydration.

A suspension of colloidal particles or of bacteria is considered to be stable, when either the repelling force, as measured by the electrokinetic potential difference, is sufficient to prevent actual contact of the particles when opportunity for their collision is presented in virtue of their Brownian motion, or the work of cohesion ($2S\gamma AB$) tending to hold these together after contact is less than sufficient to overcome the tendency for their redispersion.

The undoubted importance of the state of hydration of colloidal particles is attributed primarily to the effect of the hydrous condition of the particle surface on the particle-dispersion-medium free interfacial energy (γAB), which in turn determines the work of cohesion between the particles, ($2S\gamma AB$). The greater the state of hydration of a given surface, the more the surface resembles the aqueous dispersion medium and presumably the less the free inter-

facial energy. Therefore the greater the state of surface hydration, the less would be the cohesive force between the particles and the greater their tendency to form a stable dispersion. When a surface is altered by the deposit of another material upon it, however, no simple relation between the changes in hydration and cohesion so induced can be predicted. Certain errors are pointed out in the theory of suspension stability that has been formulated by Reiner.

In the next section, dealing with the stability of suspensions of unsensitized bacteria, it is shown experimentally that bacteria exist of a wide variety of surface types, from those which are strongly hydrophilic to those which are strongly hydrophobic. The factors determining the stability of a suspension of a given type of bacteria are shown to be those determining the stability of a dispersion of colloidal particles of the same surface type. The probable relation of surface hydration to the cohesive force of Northrop and De Kruif is pointed out.

In the final section, dealing with the stability of suspensions of sensitized bacteria, it is pointed out, on the basis of the aforementioned theoretical formulation, that the agglutination of bacterial suspensions by antibodies must be due to the fact that the antibody-globulin deposited on the bacteria by virtue of the specific combining affinity of antigen and antibody gives them surfaces which have both an electrokinetic potential difference below that of the critical value and a work of cohesion above the critical value for the antibody surface under the conditions of test. Formulations purely on the basis of "lowering of electrokinetic potential," "lowering of state of surface hydration," or increase of "cohesive force" are incomplete and misleading.

The last section gives the first experimental demonstration that adsorption of tannin on bacteria results in a surface of increased cohesiveness which is electronegative even in acid solutions. Tannin thus resembles antibodies in forming a cohesive deposit on the particles it precipitates; the tannin-treated surface, however, differs from the specifically sensitized surface in its electronegative character in acid solutions.

We are indebted to Dr. J. H. Northrop and to Dr. J. Freund for reading critically this manuscript.

Bibliography

[1] Wells: "The Chemical Aspects of Immunity," Revised edition (1929).

[2] Jones: J. Exp. Med., **46**, 303 (1927); **48**, 183 (1928).

[3] Mudd, Lucké, McCutcheon and Strumia: J. Exp. Med., **52**, 313 (1930).

[4] Bordet: Ann. Inst. Pasteur, **13**, 225 (1899).

[5] Eisner and Friedemann: Z. Immunitäts., **21**, 520 (1914).

[6] Landsteiner and van der Scheer: J. Exp. Med., **50**, 407 (1929).

[7] Goebel and Avery: J. Exp. Med., **50**, 521 (1929).

[8] Heidelberger: Chem. Rev., **3**, 403 (1926-27); Physiol. Rev., **7**, 107 (1927).

[9] Mudd and Mudd: J. Exp. Med., **46**, 167 (1927).

[10] Mudd and Mudd: J. Exp. Med., **40**, 647 (1924); Cf. also Reed and Rice: J. Bacteriol., **22**, 239 (1931).

[11] White: Medical Research Council, Sp. Rep. Ser., No. 103, London (1926).

[12] Mudd, Lucké, McCutcheon and Strumia: Colloid Symposium Monograph, **6**, 131 (1928).

[13] Shibley: J. Exp. Med., **44**, 667 (1926).

[14] Mudd and Mudd: J. Exp. Med., **46**, 173 (1927).

[15] Northrop, in Jordon and Falk: "The Newer Knowledge of Bacteriology and Immunology," Chapter LVIII (1928).

[16] McCutcheon, Mudd, Strumia and Lucké: J. Gen. Physiol., **13**, 669 (1930).

[17] Eagle: J. Gen. Physiol., **12**, 825 (1928-29); Dean: Proc. Roy. Soc., **84** B, 416 (1911-12); Leschly: Z. Immunitats., Orig., **25**, 219 (1916).

[18] Bechhold: Z. physik. Chem., **48**, 385 (1904).

[19] Tulloch: Biochem. J., **8**, 293 (1914).

[20] Buchanan: J. Bact., **4**, 73 (1919).

[21] Freundlich, translated by Hatfield: "Colloid and and Capillary Chemistry," 432;

[22] Freundlich, translated by Hatfield: loc. cit., 242.

[23] Herzfeld and Klinger: Biochem. Z., **83**, 228 (1917).

[24] Northrop and De Kruif: J. Gen. Physiol., **4**, 639 (1921-22).

[25] Northrop and De Kruif: J. Gen. Physiol., **4**, 655 (1921-22).

[26] Northrop and Freund: J. Gen. Physiol., **6**, 603 (1923-24).

[27] Kruyt, "Colloids," translated by van Klooster, (1927); Kruyt and Bungenberg de Jong: Kolloidchem. Beihefte, **28**, 1 (1929); Kruyt: ibid. **29**, 432 (1929).

[28] Bungenberg de Jong: Rec. Trav. chim., **42**, 453 (1923).

[29] Bungenberg de Jong: Rec. Trav. chim., **43**, 35 (1924).

[30] Bungenberg de Jong: Rec. Trav. chim., **46**, 727 (1927).

[31] Bungenberg de Jong: Rec. Trav. chim., **48**, 494 (1929).

[32] Reiner and Fischer: Z. Immunitäts., **61**, 317 (1929).

[33] Reiner: Z. Immunitäts., **61**, 459 (1929).

[34] Reiner and Kopp: Z. Immunitäts., **61**, 397 (1929).

[35] Freund: Proc. Soc. Exp. Biol. Med., **26**, 876 (1929); J. Immunol., **21**, 127 (1931); J. Exp. Med., in press.

[36] Neufeld and Etinger-Tulczynska: Centralbl. Bakt. Orig., **114**, 252 (1929).

[37] In this connection see, however, Mellon, Hastings and Anastasia: J. Immunol., **9**, 365 (1924).

[38] Bancroft: "Applied Colloid Chemistry," 2nd Edition, 170 (1926); Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 370.

[39] Bancroft: loc. cit., 170.

[40] Compare Kruyt, translated by van Klooster: loc. cit., 67.

[41] Kruyt, translated by van Klooster: loc. cit., 109.

[42] Freundlich, translated by Hatfield: loc. cit., 431 et seq.

[43] Freundlich, translated by Hatfield: loc. cit., 443.

[44] Harkins in Jordan and Falk: "The Newer Knowledge of Bacteriology and Immunology," 161 (1928).

[45] Harkins, Brown and Davies: J. Am. Chem. Soc., **39**, 354 (1917).

[46] Kruyt, translated by van Klooster: loc. cit., chapter XII.

[47] Kruyt, translated by van Klooster: loc. cit., 169.

[48] Cf. Seifriz in Alexander: "Colloid Chemistry," **2**, 410 (1928).; Gortner et al: Trans. Faraday Soc., **26**, 678-704 (1930).

[49] Freundlich, translated by Hatfield: loc. cit., 364.

[50] Gortner: "Outlines of Biochemistry," 190 (1929).

[51] Freundlich, translated by Hatfield: loc. cit., 418.

[52] Gortner: loc. cit., 114.

[53] Freundlich, translated by Hatfield: loc. cit., 432.

[54] Kruyt, translated by van Klooster: loc. cit., chapter XIII.

[55] Kruyt, translated by van Klooster: loc. cit., 181.

[56] Shibley: J. Exp. Med., **40**, 453 (1924).

[57] Kruyt, translated by van Klooster: loc. cit., 112.

[58] Harkins, Clark and Roberts: J. Am. Chem. Soc., **42**, 700 (1920).

[59] Loeb: "Proteins and the Theory of Colloidal Behavior," 2nd Edition, 327 (1924).

[60] Loeb: loc. cit., 342.

[61] Oliver and Barnard: Am. J. Physiol., **73**, 401 (1925).

[62] Netter: Pflüger's Archiv ges. Physiol., **208**, 16 (1925).

[63] Powis: Z. physik. Chem., **89**, 91 (1915).

[64] White: J. Path. Bact., **30**, 113 (1927); **31**, 423 (1928).

[65] Loeb: loc. cit., 349.

[66] Loeb: loc. cit., 349.

[67] Mudd and Mudd: J. Exp. Med., **43**, 127 (1926).

[68] Mudd and Kast: unpublished.

[69] Abramson: J. Gen. Physiol., **14**, 163 (1930-31).

[70] Mudd and Mudd: J. Gen. Physiol., **14**, 733 (1930-31).

[71] Cf. Michaelis in Abderhalden: "Handbuch. Biol. Arbeitsmethoden," Abt. XIII, Teil 2, Heft 2, 287 (1924).

[72] Michaelis and Davidsohn: Biochem. Z., **47**, 59 (1912).

[73] Coulter: J. Gen. Physiol., **3**, 513 (1920-21).

[74] De Kruif and Northrop: J. Gen. Physiol., **5**, 127 (1923).

[75] Shibley: J. Exp. Med., **50**, 825 (1929).

SOME APPLICATIONS OF COLLOID CHEMISTRY
IN THE SERUM DIAGNOSIS OF SYPHILIS

BY HARRY EAGLE*

It is hardly necessary to point out the importance of the laboratory procedures used in the diagnosis of syphilis. The disease is characterized by long periods of latency, during which laboratory tests are the only indication of its presence; and its active manifestations may at times simulate those of other diseases so closely as to make a differential diagnosis impossible without the confirmatory evidence supplied by a serologic examination of the blood or spinal fluid.

Two types of test are generally used. Both involve the use of an alcoholic extract of normal tissue (e.g. beef heart) as "antigen." In the flocculation tests (Sachs-Georgi, Kahn, Müller, Meinicke, etc.), this extract is diluted with a small quantity of NaCl solution, forming a milky unstable suspension consisting of the lipoids of the antigen dispersed in the aqueous phase. If this suspension is added to normal human serum, the constituent particles remain (or become) dispersed, and there is no visible aggregation; but if it is added to the serum of a syphilitic patient, there is an agglutination of the lipoid particles into visible aggregates, the formation of which constitutes a positive reaction. The second type of test is the well-known Wassermann reaction. As in the precipitation tests, the antigen is an alcoholic extract of animal tissue; but the diagnostic criterion is that a mixture of the antigen and syphilitic serum (or spinal fluid) develops the property of destroying a hemolytic component of fresh serum (complement).

The observations summarized in the following pages present no new facts or theories as regards the general field of colloidal chemistry; but they do constitute an interesting application of elementary properties of colloidal suspensions to a biological problem. Briefly, this problem is twofold: (1) What is the physical or chemical cause for the reactivity of syphilitic serum with normal tissue lipoids; and (2) how may the diagnostic tests based upon this reactivity be brought to maximum sensitivity and specificity?

I.   The Cause for the Flocculation of Tissue Lipoids by Syphilitic Serum[1]

If one drops the alcoholic extract of beef heart, hereafter designated simply as antigen, into an excess of water, one obtains a barely opalescent colloidal suspension consisting of finely divided lipoid particles. The surface properties of these particles are summarized in Figs. 1 and 2. As determined both by cataphoresis and by the zone of least stability, their isoelectric point

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is around pH $=$ 2, at which reaction there is a very slow agglutination into visible aggregates (solid portion of the curves). On the alkaline side of this isoelectric point, the particles are quite stable (broken portion of the curves). Despite the fact that N/15 NaCl suffices to reduce their cataphoretic potential to a small fraction of its original value, more than 20 times as much electrolyte is required in order to bring about their aggregation.[1] The stability of the particles is therefore not due solely to their negative electrical charge against water, but to an intrinsic hydrophilic property of the antigen lipoid.[2]
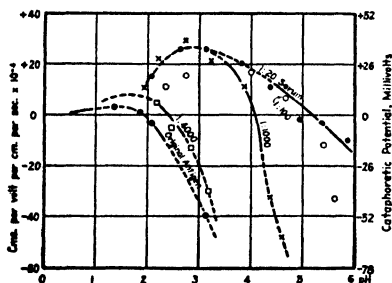
FIG. 1

The effect of hydrogen ion concentration and of normal serum upon the cataphoretic and flocculating properties of beef heart "antigen."
- - - - - stable.
————— optically visible aggregation.

FIG. 2

Effect of electrolytes upon the flocculating and cataphoretic properties of "antigen" at pH 6.0.

In the presence of normal human serum these antigen particles adsorb serum protein, which forms an incomplete film around the lipoid particles. As more and more protein is adsorbed, the zone of optimal precipitation, coinciding with the cataphoretic isoelectric point, gradually shifts to a more alkaline reaction, approaching as its maximum value pH $=$ 5, the isoelectric range of serum protein, at which point the particle is presumably completely covered by the adsorbed film (Fig. 1).

The significant feature of this adsorption is that on either side of this isoelectric point, the particles remain stable; the electrolyte concentration required to produce flocculation of the sol is not affected. Clearly, the adsorbed protein retains its water-soluble, hydrophilic properties, acting as a protective rather than a sensitizing film, and preventing even the normal flocculation of the lipoid particles at their original isoelectric point.

Quite different relationships obtain if syphilitic serum is added to the suspension. The constituent particles aggregate and sediment, leaving a

[1] In a sol containing 0.08% lipoid. The exact coagulation value depends upon the method of preparation of the antigen, the method used in preparing the sol, its concentration, the hydrogen ion concentration, the quantity of sensitizing material (see page 700), etc.

[2] The active lipoids in a tissue extract are insoluble in acetone. We have found that hydrolysis of the extract by HCl yields fatty acids, and water-soluble substances containing P and N. Presumably, therefore, lecithin constitutes the bulk of the lipoids; its numerous water-soluble groups would explain its hydrophilic properties. Since the activity of the lipoid in the serological tests is destroyed by this acid hydrolysis, as well as by prolonged saponification, it would seem that the whole molecule is necessary for serological activity.

clear supernatant fluid.   If this precipitate is washed free of serum, resuspended in water, and the surface properties of its constituent particles examined, one finds that, as in normal serum, their isoelectric point is intermediate between that of serum protein and the original value of pH = 2; at this isoelectric point there is a rapid clumping (Fig. 3).   The distinguishing property of these sensitized particles, however, is that away from this isoelectric point, the stability of the particles is determined solely by the mutually repellent surface charge.   As soon as this is repressed below a certain critical
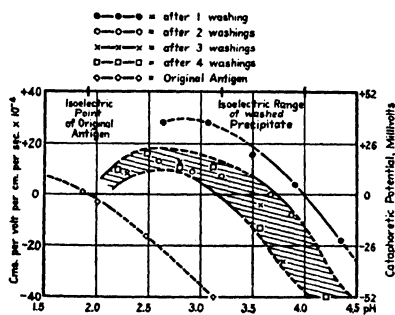
FIG. 3

Effect of hydrogen ion concentration upon the cataphoretic and flocculating properties of antigen after contact with syphilitic serum.
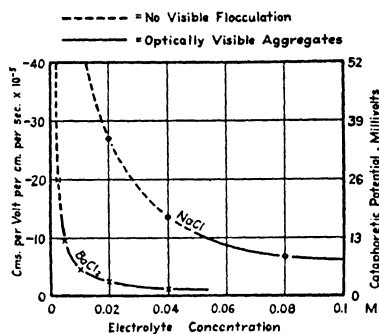
FIG. 4

Effect of electrolytes upon the flocculating and cataphoretic properties of the lipoid particles after contact with syphilitic serum.

level (10-15 millivolts), as by N/20 NaCl, the particles cohere to form visible aggregates (Fig. 4).

"Syphilitic" protein can be demonstrated in the washed precipitate both chemically (Klostermann and Weisbach;[1] Scheer[2]) and immunologically (Otto and Winkler[3]); and the specific substance in syphilitic serum is constantly associated with the globulin fraction of the serum protein (Gloor and Klinger;[4] Sahlman;[5] Kapsenberg;[6] Stern;[7] Eagle[8]).   Moreover, heating a suspension of these sensitized particles at 100°C coagulates and separates a protein film, so that one obtains particles of heat-coagulated specific protein side by side with unchanged, stable lipoid particles which can combine afresh with syphilitic serum (Georgi;[9] Eagle[10]).

[1] Deutsch. med. Wochenschr., **47**, 1092 (1921).

[2] Münch. med. Wochenschr., **68**, 43 (1921).

[3] Med. Klin., **18**, 799 (1922).

[4] Z. Immunitätsforsch., **29**, 435 (1920).

[5] Ibid. **33**, 130 (1923).

[6] Ibid. **39**, 3 (1924).

[7] Bioch. Z., **144**, 115 (1924).

[8] J. Exp. Med., **52**, 717 (1930).

[9] Z. Immunitätsforsch., **29**, 435 (1920).

[10] J. Exp. Med., **52**, (1930).

It would therefore appear that syphilitic serum contains a protein with a strong specific affinity for these lipoid particles, quite different from the attraction determining the non-specific, loose adsorption of normal serum protein. The irreversible combination of this particular protein with the antigen particles in some way deprives it of its hydrophilic properties. Instead of forming a protective, water-soluble film, it forms a film of "denatured" water-insoluble protein which is as unstable as e.g. globulin coagulated by heat, and which sensitizes the underlying lipoid particle to agglutination by electrolyte.
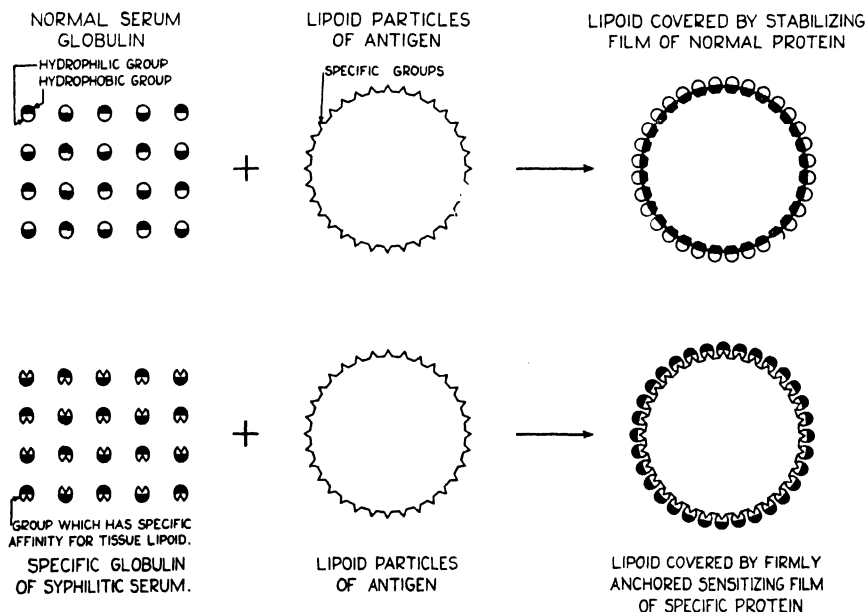
FIG. 5

Hypothetical explanation for the "denaturation" of the specific antigen-globulin at the surface of the lipoid particles.

Without going into the confusing technical details of the Wassermann reaction, it may be stated that the same film which causes precipitation is also responsible for the phenomenon of complement fixation (Eagle[1]).

I can only venture a guess as to the cause for this irreversible change in the specific globulin when it combines with the antigen lipoid. Possibly the complex protein molecule is polar, containing both hydrophilic and hydrophobic groups, the former determining its solubility in water. When normal protein is adsorbed by the lipoid particles the hydrophilic groups would naturally face the water phase, and the particle as a whole would have the stable surface properties of a dissolved protein. Perhaps in the active protein of syphilitic serum the hydrophilic groups have an even greater specific affinity for the lipoid than they do for water. In such a case, following the combination of the

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[1] J. Exp. Med., **52**, 739 (1930).

lipoid with the protein, the residual hydrophobic groups of the protein molecule would necessarily face the water phase, endowing the complex with the surface properties of "denatured," water-insoluble protein, and precipitation would naturally follow.

This hypothesis, and I wish to emphasize the fact that it is only an hypothesis, as yet not amenable to experimental test, is diagrammatically illustrated in Fig. 5.

Altogether aside from the truth or falsity of this particular theory, it is highly significant that the aggregation of antigen lipoid by syphilitic serum is entirely analogous to the aggregation of bacteria, red cells, or dissolved protein by the homologous antiserum. It suggests the possiblity that the active protein in syphilitic serum represents an antibody to products of syphilitic infection, presumably the Treponema pallidum.

II.   The Explanation of the Sensitizing Action of Cholesterol[1]

It has been known for many years that the addition of cholesterol to an alcoholic extract of normal tissue causes a very great increase in its sensitivity in the diagnostic tests for syphilis, despite the fact that cholesterol as such is quite inactive. We believe the following to be an adequate explanation of this phenomenon.

When the cholesterolized antigen is dropped into an excess of NaCl $N/7$, it forms a stable colloidal suspension similar to that formed by antigen alone, but somewhat more opalescent. Many more particles are visible by dark field examination, but there are no coarse sedimenting aggregates such as appear if an alcoholic solution of cholesterin is dropped into salt solution.

This effect of the tissue lipoids in causing a stable colloidal dispersion of hydrophobic cholesterol is considered analogous to the detergent action of soap upon particles of dirt. When the alcoholic solution of tissue lipoids and cholesterol is diluted with water, the immediate tendency of the cholesterol is to cohere into coarse crystalline sedimenting aggregates, exactly as it does when its alcoholic solution is dropped into water. While the cholesterol particles are still of colloidal dimensions, however, it is believed that they adsorb the surface-active lipoids of the antigen, which have a lower interfacial tension against water and which act as a protective colloid, preventing any further cohesion. The suspension remains of colloidal dimensions and therefore stable. The antigen-covered cholesterol particles are now to all intents and purposes particles of pure antigen (Fig. 6).[1]

There is ample confirmatory evidence that this is the cause of the stable suspension formed by a cholesterinized antigen. The isoelectric point of the particles it forms is around pH2, the same as that of antigen particles, and approximately $M/1$ NaCl is necessary to bring about their flocculation in a dilute suspension. In marked contrast, cholesterol particles have no definite isoelectric point, and are so hydrophobic that they precipitate even in water, despite a very high surface charge (> 100 millivolts). Many other hydrophobic

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[1] Figs. 6 and 7 are reproduced from J. Exp. Med., **52**, 747 (1930).

substances, which normally form coarse aggregates when their alcoholic solution is dropped into water, are brought into colloidal "solution" by the addition of tissue lipoids to the alcoholic solution. Conversely, many other surface-active substances, such as serum, Na-oleate, Na-taurocholate, etc., cause a colloidal dispersion of cholersterol if its alcoholic solution is dropped slowly with shaking into an aqueous solution of these surface-active substances.

The more cholesterol is added to the antigen before diluting with saline, the coarser are the individual particles of the sol obtained, the more are visible by microscopic examination, and the greater is the opacity of the sol. Presumably, this is due to the fact that the aggregation of the cholesterin is more rapid at higher concentrations, allowing the aggregates to become larger before they adsorb a completely protective film of antigen-lipoid (Fig. 7).
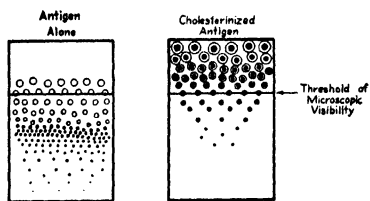
Fig. 6

Diagrammatic representation of the effect of cholesterol in causing a coarsened dispersion of the antigen sol.
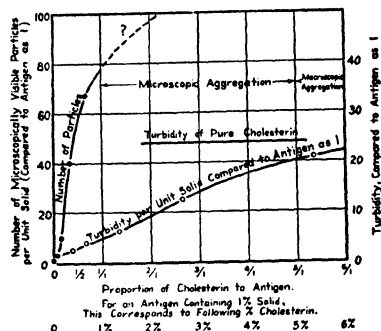
Fig. 7

Effect of cholesterin upon the turbidity and the number of microscopically visible particles in an antigen sol.

The effect of cholesterol is increasing the sensitivity of the antigen, illustrated in Fig. 7, is not due to the cholesterol as such, but to the coarsened dispersion of the antigen-lipoids which it causes. For obvious reasons the larger particles formed by a cholesterolized antigen are easier to agglutinate into visible aggregates. Moreover, although there is no satisfactory explanation for the observation, it can be shown that such large particles have a much greater affinity for the specific protein of syphilitic serum than similar particles of smaller size. Thus, if one drops antigen into an excess of saline, one obtains a finely dispersed, barely opalescent lipoid sol: if, using the same quantities, one drops the saline to the antigen, a much coarser solution is obtained, similar to the solution produced by a cholesterolized antigen. Despite the fact that the particles of the former sol have a much greater total surface area, the latter is far more effective in the Wassermann reaction. The greater sensitivity of the cholesterolized antigen in both the precipitation and complement fixation tests is therefore believed to be due, in part at least, to the fact that the average particle in the aqueous dilution is larger than the particles formed by pure antigen.[1]

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[1] An additional factor may be an orientation of the adsorbed lipoid molecule on the surface of the cholesterin, presenting specific reacting groups to the aqueous phase.

III

We now come to an important practical application of the foregoing discussion. If cholesterol owes its activity solely to the fact that it causes a coarser dispersion of the antigen lipoid by acting as an inert core onto which the active lipoid is adsorbed, then (1) it should be used up to the limit of its solubility in alcohol, and (2) any substance which because of a lower surface tension against antigen lipoid than against water, would adsorb the antigen lipoids in an aqueous phase, should have a similar sensitizing action.

A large series of water-insoluble, alcohol-soluble substances were tested; and with only a few exceptions they all had qualitatively the same effect as cholesterol. Added to the alcoholic extract, they caused a coarsened dispersion of the antigen lipoid when the extract was diluted with water; and when this dilution was tested for its sensitivity in the Wassermann reaction, it was found to be more sensitive that the original antigen. Some of the substances are grouped in Table I in the order of their sensitizing efficiency.[1]

The use of the best of these sensitizers as adjuncts to cholesterol has enabled us to develop a Wassermann antigen which is considerably more sensitive than any hitherto available. The particular substances used are sitosterol and a sterol derived from wool.

TABLE I[2]

Sensitizing Efficiency of the Various Alcohol-Soluble, Water-Insoluble
Substances tested

Slight	Fair	Very good
Gum guaiac	Gum balsam	Cholesterol
Gum sandarac	Gum copal	Sitosterol
Salol	Gum mastic	Wool Sterol
Gum shellac	Gum elemi	Corn Germ Sterol
Resin	Tolu balsam	Gum thus
Benzoin	Benzophenone	Safrole
Terpineol	Aurin	Diphenyl
Benzil		Dimethyl naphthylamine
p-iodobenzene		Methyl stearate
Ethyl-m-nitrobenzoate		Methyl palmitate
β-Chloronaphthalene		
Triphenyl phosphine		
d-Naphthonitrile		
p-nitrobromobenzene		
Ethyl palmitate		
p-Bromotoluene		

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[1] Possibly, the sensitizing efficacy of these substances depends upon the magnitude of the expression

$$\text{Interfacial tension} \quad \text{interfacial tension} \quad - \text{ Interfacial tension}$$
$$\text{substance} \times \text{water} \quad \text{antigen} \times \text{water} \quad \text{substance} \times \text{antigen}$$

The greater this difference, the more avid would be the adsorption of the active lipoid by the microscopic aggregates of the sensitizer. Unfortunately, the first term cannot as yet be determined experimentally.

[2] Reproduced from J. Exp. Med., 53, 605 (1931).

Flocculation tests, because of the simplicity of reagents and of technique, as contrasted with the laborious complexity of the Wassermann reaction, would greatly simplify the serological diagnosis of syphilis were it not for the too great personal factor involved in the interpretation of end results with minute degrees of aggregation. The addition of corn germ sterol in the proper proportions to a cholesterolized antigen to a great extent removes this objection. A new flocculation test based on its use has been devised and is now in routine use at the Johns Hopkins Hospital. The apparent superiority of the test is considered to be due to the fact that when this antigen is diluted with salt solution, it forms a colloidal suspension consisting of comparatively large needle crystals of sterol covered with a film of the active lipoid, instead of the minute amphorphous particles formed by a cholesterolized antigen. Despite the fact that these needles are sufficiently large to be seen as a cloud of refractile particles when the suspension is shaken, the mixture of normal serum and antigen is extremely stable, remaining translucent and showing no gross sedimentation or microscopic aggregation even after 24 hours. Upon addition to syphilitic serum, however, the crystals combine with the specific protein as already described, and subsequently clump to form granular aggregates of crystals readily visible to the naked eye and under the microscope; upon centrifugalization, these form large coherent clumps. Properly performed, the test is very sensitive, and allows for a sharp differentiation between syphilitic and normal serum.

Summary

1. Observations on the aggregation of an aqueous suspension or beef heart lipoids (antigen) by syphilitic serum indicate that the phenomenon is wholly analogous to the aggregation of bacteria, red cells or a dissolved antigen by the homologous antiserum. The mechanism of the reaction is conceived to be as follows. A specific component of syphilitic serum, associated with the globulin fraction of the serum protein, is firmly bound onto the surface of the individual particles of the lipoid sol, forming a sensitizing film of denatured hydrophobic protein quite unlike the stabilizing film formed by adsorbed normal serum protein. The original particles, immersed in water or normal serum, are stable because of an inherent hydrophilic property of the surface; while the stability of the sensitized particles is determined by their charge against water. When this mutually repellent charge is depressed below the critical value (10-15 millivolts) by electrolytes, the particles cohere to form optically visible aggregates.

The same film which causes aggregation also adsorbs complement, giving the Wassermann reaction of complement fixation.

2. This complete analogy to the truly specific antigen-antibody reactions suggests that the reactivity of syphilitic serum with normal tissue lipoids may be due to the presence in such serum of antibodies to as yet uncharacterized products of infection.

3. The effect of cholesterol in increasing the diagnostic efficiency of the antigen is considered due to the fact that when the cholesterolized antigen is

dropped into water, microscopic aggregates of cholesterol in statu nascendi adsorb the serologically active antigen lipoid, forming particles which are many times larger than those formed by the antigen lipoid alone. This coarser dispersion is much easier to agglutinate; moreover, the larger particles have an unexplained greater affinity for the specific component of syphilitic serum. Both these factors would account for the greater sensitivity of the cholesterolized antigen in the diagnostic tests.

4. This explanation of the sensitizing action of cholesterol led to the search for substances which might have a similar affect. Of the numerous such substances found, sitosterol and sterols derived from corn germ and wool have proven of practical importance. Their use as adjuncts to cholesterol causes a significant increase in the sensitivity of the Wassermann antigen; while the physical properties of the corn sterol have led to the development of a new flocculation test for syphilis of great simplicity and sensitivity.

Syphilis Division,
Department of Medicine,
Johns Hopkins Medical School,
Baltimore, Md.

THE COUPLED NATURE OF LACTIC ACID-GLYCOGEN SYNTHESIS IN MUSCLE

BY DEAN BURK[*]

The view developed so largely by Meyerhof and Hill that the synthesis of glycogen or carbohydrate from lactic acid in isolated muscle requires energy derived from the oxidation of such compounds has been questioned recently by Bancroft and Bancroft,[1] who have attempted to demonstrate that the formation of glycogen from lactic acid can be explained equally well upon other grounds. They suggest that a reversible equilibrium exists between the two compounds which may be disturbed by extraction of glycogen from solution by adsorption on muscle protein, thereby causing further formation of glycogen. This implies that the free energy of the synthesis is small, or at times zero.

It will be shown here that the Bancroft and Bancroft reversible equilibrium explanation is quantitatively inconsistent with the existing available thermodynamic free energy data.[2] Although aware that "the equilibrium point of this reaction is well over on the lactic acid side" it would appear that these writers failed to appreciate the quantitative completeness of the spontaneous breakdown, as will be evident immediately upon consideration of the free energy data.

From data given elsewhere,[3] in a form somewhat different[4] from that employed here, however, the free energy of the following synthesis, as it is normally considered to occur in muscle,

lactate ion (0.002 M = 0.018%) + H$^+$ (2.5 × 10^{-8}, or pH 7.6) = n glycogen (1%)   (1(

is 393 cal/gm., or 35370[5] cal/mol of lactic acid (the heat of reaction is 268 cal/gm., or 24120 cal/mol). Correspondingly, at pH 3.28, where the free

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[1] J. Phys. Chem., 35, 194 (1931).

[2] Bancroft and Bancroft state: "The extent of this coupled reaction is remarkable, for Hill has shown that under suitable conditions the ratio of the amount oxidized to the amount synthesized is one to five or one to six." The ratio actually corresponds to an efficiency of 100 × (5/(325000/35370)), or 46%, where − 325000 cal. is the approximate free energy of combustion of lactic acid under physiological conditions. As a matter of fact, the writer has recently indicated (J. Phys. Chem., 35, 432-56 (1931)) that the coupled autotrophic reduction of carbon dioxide by hydrogen has an efficiency of substantially 100% when (as in the glycogen synthesis just considered) the extraneous maintenance energy of the biochemical machine accomplishing the reaction is neglected. Several other fairly highly efficient reactions were likewise discussed, and also a considerable number of reactions with efficiencies of 20-50%.

[3] Burk: Proc. Roy. Soc., 104B, 153-170 (1929).

[4] Entropy changes rather than free energy changes received chief expression.

[5] In accordance with convention, the accuracy of free energy values is not indicated by the number of significant figures given.

energy of neutralization is zero at the concentration of lactic acid considered, the free energy of the synthesis

$$\text{lactic acid } (0.002 \text{ M}) = n \text{ glycogen } (1\%) \qquad (2)$$

is 336 cal/gm., or 30240 cal/mol of lactic acid (the heat of reaction is $-$ 180 cal/gm., or 16200 cal/mol). n is the reciprocal of the ratio of the molecular weight of glycogen to that of lactic acid, and its significance will be considered later.

Bancroft and Bancroft's statement "From a purely chemical point of view this reaction (lactic acid-glycogen synthesis) should not require much energy" is obviously untrue; on account of the very large free energy requirement (a positive value of 35370 cal.) it is inconceivable that reaction (1) as written could occur spontaneously in muscle, at least in experimental, physiologically significant quantity. The question might remain, however, as to how far Bancroft and Bancroft would agree that Equation (1) represents approximately the essential conditions, particularly of concentration, of the reaction taking place in muscle.

They affirm (within $\pm$ 10-fold) the adopted and generally accepted concentration of 0.002 M lactic acid dissolved in the plasma of fresh, isolated muscle.[1] It may be pointed out that for every 10-fold dilution or concentration of lactic acid the free energy of Equation (1) becomes changed respectively $\pm$ 1365 cal., i.e., changed to 36735 or to 34005 cal., respectively. Correspondingly, for every $10^x -$ fold dilution or concentration, the free energy becomes changed by approximately x 1365 cal. Hence for equilibrium conditions to prevail (i.e., for $\triangle$ F to equal zero) the activity (or approximate concentration) of lactic acid would have to be maintained at the impossible figure of 0.002 $\times$ $10^{(35370/1365)}$ M, or ca. 10^{23} M. Even neglecting neutralization, which normally takes place more or less completely under physiological conditions, and considering glycogen formation according to Equation (2), as might occur independently of muscle, the figure remains still as high as 0.002 $\times 10^{(30240/1365)}$ M, or ca. 10^{20} M.

Likewise, it can easily be shown that adoption of physiological pH values other than 7.6 would influence the figure of 35370 cal. in Equation (1) but relatively little. At pH 6.9, for instance, it is reduced by only 990 cal. to 34380 cal.

With respect to the concentration of glycogen, Bancroft and Bancroft have introduced one new factor hitherto considered but little. They assert (as may very well be the case) that the 1% glucogen in muscle does not exist in solution but is almost completely adsorbed on muscle protein, the adsorption being reversible. In other words, the concentration of glycogen to be reckoned with in Equation (1) is not 1%, but something like 0.01%, or even less, i.e., there obtains an adsorption of 99% or more. They state qualitatively, "the reaction can be forced back from lactic acid to glycogen by the adsorption of glycogen out of solution on the protein, thereby reducing the amount of free glycogen in solution and causing the formation of more to re-

[1] This value would in their view represent the approximate normal *equilibrium* concentration of lactic acid in the muscle system at rest.

establish the equilibrium." However, as shown in the manner above with lactic acid, a physiologically inconceivable, great reduction in the concentration of free glycogen would be required, $10^{(35370/1365)}$-fold, or 10^{26}-fold, even granting for the moment that the value of n in Equation (1) is unity. Assuming a value of $n = 1/1000$, the concentration reduction required would be $10^{(35370/1.365)}$-fold, or ca. 10^{26000}-fold, to $10^{-26000}\%$. As shown before (loc. cit.), owing to the very small value of n (1/100 to 1/1000), the free energy of dilution of glycogen is substantially zero for all physiological concentrations, as may be seen from the formula:

$$\triangle F_{\text{dil}} = n \text{ RT } \ln(1\%/y\%) = 1.365 \log (1\%/y\%). \tag{3}$$

where y is the physiological concentration to be considered, and n is taken to be $1/1000$. Thus, where $y\%$ is 0.001% (instead of 1%), $\triangle F_{\text{dil}}$ becomes only -4 cal. This 1000-fold dilution of glycogen decreases 35370 by only $100 \times (4/35370)$ or ca. $.01\%$, leaving reaction (1) substantially as spontaneously unreversible as before. Therefore the reversible equilibrium explanation is in disagreement not only with existing free energy data, but also with *a priori* mass law considerations of the relative molecular weights of glycogen and lactic acid. This *a priori* argument is not necessarily so important, however, since the problem of sugar synthesis from lactic acid involves a large positive free energy in the same way that glycogen synthesis does, and yet in sugar synthesis n is $1/2$, i.e., not far from unity.

As a corollary to the above reasoning it follows that the free energy of glycogen adsorption on protein is totally insufficient to account for the synthesis, since the adsorption[1] is never complete enough, i.e., it is never so complete that about less than 10^{-25999} mg. glycogen per gram of muscle plasma is unadsorbed. Moreover, as just pointed out with respect to free energy relationships, sugar synthesis is similar to glycogen synthesis qualitatively and quantitatively, so that for sugar synthesis to take place (in the absence of simultaneous glycogen synthesis) postulation of adsorption on protein and removal from solution would likewise be required, as in the case of glycogen synthesis. Whether such adsorption takes place to a great extent in the ordinary sense is questionable; in the sense required by calculations similar to those given with respect to glycogen, it unquestionably does not take place.

It should be recalled that refutation of the reversible equilibrium explanation had been accomplished more or less successfully by Meyerhof and others on the basis of heat of reaction, rather than free energy of reaction, data. Obviously, however, a critical and ultimate decision must rest upon free

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[1] The adsorption is of course itself a reversible process, according to Bancroft and Bancroft, so that the calculations of the previous paragraph with respect to glycogen concentration could be based upon either that amount in free solution or that amount adsorbed with exactly the same results or final conclusions. Since, however, in order to employ the latter method, the free energy of adsorption would have to be known (and added to that of Equation (1)) it is obviously much more convenient, and in the present state of knowledge essential, to proceed as has been done.

energy data.[1] The calculations required to produce the data given here were carried out with considerable precision; so far as the writer is aware, no assumptions were employed which if arbitrarily but judiciously changed would greatly decrease or enhance the large positive free energy value of lactic acid-glycogen synthesis in muscle given.

Bancroft and Bancroft concern themselves more with the details of gly-cogen-lactic acid breakdown than with lactic acid-glycogen synthesis. Owing to the long-established spontaneous nature of the breakdown, the really deciding test of the freely reversible equilibrium explanation must *now* concern itself with the synthesis; for this reason the present paper is considering chiefly the synthesis.[2] It may be pointed out with respect to the breakdown, however, that if lactic acid were in equilibrium with glycogen just before a muscle at rest were stimulated, the free energy of the breakdown subsequently called forth by stimulation would, per mol of lactic acid, be so close to zero as to be totally incapable of accounting for the work performed in any contraction of appreciable duration. So far as is known at present, the anaerobic performance of mechanical work derives its free energy *ultimately* from glycogen-lactic acid breakdown; this statement needs no qualification with respect to the finding within the last year or two that a certain amount of mechanical work may be obtained under conditions where lactic acid formation is prevented by iodo-acetic acid poisoning. Although other reactions may even under normal conditions be more immediately responsible for the performance of mechanical work than glycogen-lactic acid breakdown, presumably the latter is normally required later to reverse the other reactions so that they may then re-perform work.

Bancroft and Bancroft state: "If this is in reality a coupled reaction, one should be able to take lactic acid, oxidize it in the presence of protein, and form glucose." This is not necessarily true; one or more of the intermediate processes may require enzymatic catalysis. A coupled reaction need not, by

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[1] It is interesting to note, also, that upon the basis of the free energy data given in this paper, the possibility suggested by Kluyver (Archiv. Mikrobiol., **1**, 181 (1930)) is likewise precluded, that in glycogen synthesis from lactic acid the mechanism proceeds by way of pyruvic acid and acetaldehyde. In such an event, from stoichiometric considerations alone, no more than two molecules of lactic acid could disappear in synthesis, per one molecule burned, whereas (see p. 2) theoretically ten are possible, and experimentally five have been observed. The theory of the mechanism involving passage through a 2-carbon molecule stage (such as acetaldehyde) can not be true, therefore. Escape from this conclusion can involve only the hypothesis that the numerous, and variously performed experimental measurements of the ratio have been incorrect, or wrongly interpreted.

[2] It is beyond the scope of this paper to trouble to prove that not only does lactic acid-glycogen synthesis in muscle require a large amount of free energy but also that this free energy is supplied by oxygen consumption. It need scarcely be mentioned that no anaerobic reaction in muscle is known capable of providing such a large amount of free energy for the large amounts of synthesis which may on occasion take place. Although not inconceivable that very small, substantially unmeasurable amounts of synthesis might take place through energy provided by some anaerobic reaction, possibly incidental to the mechanism, this would be beside the point, since we are interested here in explaining the large synthesis transformations observed experimentally.

Bancroft and Bancroft state: ". . . the oxidation of lactic acid is not coupled with the synthesis of glycogen, but occurs simultaneously in the presence of oxygen," but offer no explanation for the fact that synthesis does not occur in the absence of oxygen. Likewise they do not explain, even on the basis of their theory, how stimulation causes elution of glycogen from protein.

its very nature, invariably proceed in the absence of an enzyme. Exception must be taken to Bancroft and Bancroft's conception of coupling as excluding enzymatic action, at least so far as the term coupling has been employed by physiologists with respect to the synthesis under discussion.

In view of Equations (1) and (2), it is not at all surprising that Bancroft and Bancroft failed in an experimental attempt to show that glycogen could be formed from lactic acid when "Using 15 cc. of a .2% solution of d-lactic acid, 10 cc. of M/2 KH_2PO_4, and 10 cc. of enzyme solution, and approximately 30 grams of egg white. . . ." In any such future attempts, great caution will have to be exercised in evaluating positive results, i.e., in excluding all other possible reactions, particularly oxygen consumption, which might be responsible for providing the necessary free energy or equilibrium point shift. Indeed, on account of the great heterogeneity of the system in which the synthesis would have to be carried out, the formation only of considerably more than traces of glycogen could give rise to the suggestion that the thermodynamic data given here are inadequate or inapplicable.

Summary

1. The theory recently suggested by Bancroft and Bancroft that in muscle glycogen may be synthesized from lactic acid according to a freely reversible shift in the equilibrium point caused by adsorption of glycogen out of solution is shown to be quantitatively inconsistent with both (1) the existing thermodynamic free energy data and (2) *a priori* mass law considerations. The theory is also shown to be unable to account for the production of mechanical work in muscle upon the basis of free energy derived from glycogen-lactic acid breakdown.

2. The failure of Bancroft and Bancroft to accomplish the synthesis experimentally *in vitro* is in accord with the prediction of thermodynamic data given in this paper, according to which one milligram of glycogen would form spontaneously in not less than some billion trillion liters of a .2% solution of lactic acid; in fact, owing to the high molecular weight of glycogen, a vastly greater volume of such a solution would be required.

IRRITABILITY AND ANESTHESIA IN PLANTS*

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.[1]

That mysterious thing called protoplasm is acknowledged to be the essential component of living things, being directly associated with the properties by which man is able to distinguish the living state, namely respiration, growth, reproduction, movement, and irritability. Proteins are integral constituents of protoplasm. Provided one does not adhere to an exclusively rigid set of conditions by which to characterize the state of anesthesia, all living things, then, can be anesthetized. According to no less an authority than Claude Bernard,[2] "the action of anesthetics is very general. They react not only with animals but also with plants."

Many cases illustrate this: i.e., mammals by ether, fish by urethane, yeast cells by alcohol, frogs by cold, trypanosomes by arsenic, various bacteria by chloroform, various plants by ethylene, etc.

A natural consequence of these facts is the strong suspicion that the reversible coagulation theory of anesthesia should be applicable to plants. One finds further assurance that this is the case in the words of Bose:[3] "In surveying the response of living tissues we find that there is hardly any phenomenon of irritability observed in the animal which is not also found in the plant. The various manifestations of irritability in the plant have been shown to be identical with those in the animal. The study of the responsive reactions in plants must, therefore, be regarded as of fundamental importance in the elucidation of various phenomena relating to the irritability of living tissues."

Bose and Das,[4] partly because of the conduction of impulses by *Mimosa pudica*, take the stand that the plant contains conducting or nervous tissue. Many plant physiologists oppose this idea rather violently, however. Whether or not plant tissue is so highly differentiated as to contain a nervous system makes little difference; the important thing appears to be that there is some sort of parallelism between the plant and animal kingdoms as regards the conduction of a stimulus. In his earlier work Bose[5] found that *Mimosa* is excited upon the application of electric current in a manner which is entirely comparable to animal nerves. For instance, in both the muscle of a frog and in *Mimosa* fatigue under continuous stimulation is found to take place. Likewise there is a preliminary staircase response under successive stimulations which is followed by fatigue both in the frog muscle and in *Mimosa*. The graphic record of these responses is strikingly similar in the two cases.

[1] Eli Lilly Research Fellow.
[2] "Leçons sur les anesthésiques et sur l'asphyxie" (1875).
[3] "Researches on Irritability of Plants," 360 (1913).
[4] Proc. Roy. Soc., **98B**, 290 (1925).
[5] "Researches on Irritability of Plants" (1913).

Herbert[1] even goes on record to the effect that there is no anesthesia in plants, basing his case on work done with the sensitive plant (*Mimosa pudica*). The grounds upon which he bases this idea are not clear; in the end the matter is evidently only one of terminology.

Using wild sorrel leaves and hyacinths Lumière and Couturier[2] claim to have produced anaphylaxis in plants, the antigen being horse serum. The anaphylactic response was evidenced by the death of the plant several days after the shocking dose of antigen was injected. Onion bulbs were likewise subject to what Lumière designates as anaphylaxis; here monkey serum was the antigen. Picado[3] claims to have demonstrated the formation of antibodies to foreign proteins injected into cacti of the genus Opuntia. These views are opposed by Lougo[4] who concludes that one can only have anaphylaxis in animals. Call it what you may, it is doubtless true that there is a response in certain previously sensitized plants to the injection of foreign proteins. It seems better at the present time to steer clear of the conception that anaphylaxis occurs in plants; the important point nevertheless is that both plants and animals respond, in their own way of course, to foreign proteins.

These things of course do not make a plant into an animal, but they do provide a rational basis for the assumption that the reversible coagulation theory of anesthesia should apply in principle, if not in detail, to plants.

Changes in turgor are, according to Mathews,[5] responsible for movements in many plants, an example of this principle being the sensitive plant. Mac-Dougal[6] extended this idea to cover the growth of plants. Supporting his theory that plant protoplasm is a colloidal system of a pentosan, albumin, and soap he found that compounds which promote growth in plants increased the hydration capacity of such a mixture. In another paper MacDougal[7] reports that calcium chloride solutions induce the maximum swelling of gelatin in 0.001 M concentration, whereas the hydration is cut down as the concentration of calcium chloride increases or decreases from this optimum.

In animals the cycle, normality, irritability, anesthesia, irritability, normality, has been observed repeatedly with a variety of anasthetics.[8] There is much that indicates a similar response to anesthetics by a variety of plants. Lepeschkin[9] found that the fading of the corolla of *Chicorium Intybus* under the influence of narcotics cannot be brought about by the formation of a poisonous substance in the cells. Low concentrations of narcotics prolonged the life, but higher concentrations accelerated the fading. The significance of this work would have been greater had the author correlated his facts better, for he found that protein denaturation is the cause of heat fading. Yet he

[1] Philippine Agriculturist, **11**, 141 (1922).
[2] Compt. rend., **172**, 1313 (1921).
[3] Ann. inst. Pasteur, **35**, 893 (1921).
[4] Lougo and Cesaris-Demel: Chem. Abs., **10**, 3294 (1925).
[5] "Physiological Chemistry," 205 (1915).
[6] Am. J. Bot., **8**, 296 (1921).
[7] Proc. Am. Phil. Soc., **60**, 15 (1921).
[8] Bancroft and Rutzler: J. Phys. Chem., **35**, 1185 (1931).
[9] Am. J. Bot., **16**, 324 (1929).

does not mention the relation between this and the fading due to narcotics. Nichols[1] is more helpful. He applied chloroform to the wall of an internode of Nitella by means of a capillary pipette. As the point of application of the anesthetic an area of non-motile protoplasm was produced. This area of non-motile protoplasm ultimately resumed movement; thus the process appears to be a reversible one. Nichols considers that the effect of the chloroform is due to gelation; this provides us with a definite case of reversible coagulation in plants accompanied by anesthesia of the part affected.

Magnesium sulphate is a well-known anesthetic and might therefore be expected to act as such for plants. Canals[2] found that above five parts of magnesium sulphate per 10,000 parts of water the compound is toxic to the roots and stems of plants. Magnesium sulphate in less concentrated solutions has a stimulating ("favorable") action on the stems. Distilled water can be used as a local anesthetic,[3] and Heilbrunn[4] found that the protoplasm of the eggs of sea-urchins can be coagulated by distilled water. It is not surprising to find, therefore, that distilled water exerts a toxic action on plants.[5] It was found that the action is not always stopped by adding salts; it depends upon what salts are added and upon their concentration. Heat and mechanical coagulation of proteins are not new phenomena. Herbert[6] recognized that heat produces an excitatory fall in *Mimosa* resembling in all respects that produced by mechanical shock. Wallace,[7] in a recent paper, made a quantitative study of the effect of temperature upon the sensitive plant by measuring the angle of movement of the branches at different temperatures. Some of his data follow. The data show three very interesting things; the sensitivity of *Mimosa* is lost at 60°, which is about the coagulation temperature of albumin; coagulation by cold is shown at 12.5°, a temperature at which there are no ice crystals present, and the temperature of maximum activity is approximately that of the animal body. Egg albumin may be coagulated

TABLE I

Temperature °C.	Degrees Angle of Movement	Temperature °C.	Degrees Angle of Movement
12.5	0.00	40.0	81.3
14.0	4.1	45.0	75.7
16.0	10.3	47.5	56.5
20.0	32.3	50.0	38.1
25.0	54.6	55.0	21.6
30.0	69.3	60.0	±0.00
35.0	75.7		

[1] Bull. Torrey Bot. Club, **57**, 153 (1930).
[2] Chem. Abs., **15**, 2654 (1921).
[3] Wyeth: N. Y. Med. J., **1906**, 6.
[4] Biol. Bull., **39**, 307 (1920); Exp. Zool., **30**, 211 (1920).
[5] Lesage: Chim. et Ind., **15**, 281 (1926).
[6] Philippine Agriculturist, **11**, 141 (1922).
[7] Am. J. Bot., **18**, 293 (1931).

reversibly by cooling,[1] and frogs may be made completely insensitive to external influences[2] by putting them in water at nearly o°. Likewise they undergo a heat narcosis in very warm water. The parallelism between plants and animals in their reponses to heat and cold coagulation seems most striking.

Tadokoro[3] made a very interesting study of the colloid chemistry of plant plasma using the press juice from macerated wheat sprouts. The chlorides of aluminum, magnesium, calcium, strontium and barium were found to flocculate the colloidal suspension, the order of the cations being: Al > Ba > Sr > Ca > Mg. Certain monovalent cations peptized the suspension in the following order: K > NH$_4$ > Na. So far as these series go, they are the same as the series for egg albumin. How much the peptizing action of KCl, NH$_4$Cl and NaCl is due to the chloride ion does not show up. It seems certain that at some point in the series the peptizing action of the anion must overbalance the coagulating effect of the cation. Salt concentrations which poison wheat were found to cause colloidal changes in the press juice. Using the following salt pairs, NaCl-CaCl$_2$; KCl-CaCl$_2$; KCl-MgSO$_4$; K$_2$SO$_4$-MgCl$_2$; and CaCl$_2$-MgCl$_2$ Tadokoro showed that in each pair there was a colloidal antagonism. These experiments were paralleled by pot culture experiments which showed a corresponding effects of the same pairs on the growth of the wheat plant. Peptone coagulated the press juice whereas glucose peptized it. Glucose and CaCl$_2$ were then found to be mutually antagonistic as well as KCl and peptone. The conclusion was drawn that the essential cause of the antagonism lies in the maintenance of a certain optimum degree of colloidal dispersion. For example, sodium chloride tends to peptize and calcium chloride tends to coagulate, so that the proper balance between them maintains the optimum dispersion.

Loew[4] found that potassium iodide, manganous sulphate, ferrous sulphate, and sodium nitrate all stimulate the growth of plants. This brings up the question of irritability or stimulation to which the theory of reversible coagulation in living tissue appears to be, in part at least, applicable. Bose[5] found that on bringing a highly excited sensitive plant into a dark room its excitability disappeared. The *Mimosa* is fully sensitive at night, however, and in the dark room its sensitivity slowly reappeared. Thus it appears that the colloidal equilibria of the plant are very delicately balanced and easily upset. Absorption of water also depressed the excitability of *Mimosa*. It was then found that glycerin restored the excitability of the plant; according to Bose this feat was not necessarily accomplished by the removal of water from the plant by the glycerol. Even though the continuous application of glycerol did not later cause a decline in the sensitivity, it does not seem improbable that it acts as a peptizing agent for the colloids of *Mimosa*. Sodium nitrate hastens

[1] Bancroft and Rutzler: J. Phys. Chem., **35**, 151 (1931).

[2] Claude Bernard: "Leçons sur les anesthésiques et sur l'asphyxie" (1875).

[3] Chem. Abs., **14**, 960 (1920).

[4] Chem. Ztg., **48**, 391 (1924).

[5] "Researches on Irritability of Plants," 87 (1913).

the sprouting of dormant potato tubers.[1] This effect may be due to two factors neither of which seems to be excluded. The nitrate ion, being a peptizing agent for proteins, probably acts in that manner with the potato tubers. Also, plants can utilize nitrates in their food economy. In a later paper Denny[2] reported that ethylene chlorhydrin and sodium thiocyanate hasten the sprouting. Employing different concentrations of sodium thiocyanate the amount of germination was greatest with a $1/2\%$ solution, being less with a 1% solution, and still less with a 2% solution. In comparison with ethylene chlorohydrin, sodium thiocyanate may be a more powerful germinating agent. The temperature at which the tubers were soaked was less important when using sodium thiocyanate, and with this compound higher temperatures could be used. For breaking the dormant period ammonium thiocyanate was found[3] to be better than sodium thiocyanate. There was not much margin between the stimulative and toxic dosages in the cases of sodium and potassium thiocyanate. Denny also found that ethyl iodide and o-tolylthiourea hastened sprouting. It requires no stretch of the imagination to class these compounds as peptizing agents. Analysis of the tissues[4] from potato tubers after treatment showed no difference between the moisture content of treated and untreated tissue. This implies that the ethylene chlorhydrin and sodium thiocyanate did not act through a change in bound water in this particular case. In another paper[5] Denny and Stanton report that the dormant period of the lilac can be broken by treatment with ether or chloroform. Ethylene in a concentration of one part per 100 when applied for 3 days to the flowering almond caused early blooming. They say that treatment with ethylene chlorhydrin or with ethylene dichloride breaks the rest of many plants and causes the flowers to come out.

It would appear at first sight that from the point of view of reversible coagulation the theory of the breaking of the rest period of plants is in a somewhat garbled state since both peptizing agents and coagulating agents accomplish the result. It is not entirely foreign to the realm of reason that one coagulating agent acting upon the same substrate may relieve the action of another coagulating agent. For instance, Stark[6] obtained good results when combating neuritis with sodium iodide, an excellent peptizing agent. However, coagulating agents such as arsphenamine are also used[7] with the production of beneficial effects. If we make the plausible assumption that in the dormant state the plant colloids are in an agglomerated condition the whole thing straightens out nicely. The action of certain coagulating agents would then be to displace the things causing the dormancy, the necessary condition being that the displacing compound shall be more strongly adsorbed, but not so

[1] Denny: Am. J. Bot., 13, 122 (1926).
[2] Am. J. Bot., 15, 395 (1928).
[3] Denny: Am. J. Bot., 13, 386 (1926).
[4] Am. J. Bot., 16, 326 (1924).
[5] Am. J. Bot., 15, 327 (1928).
[6] Neb. State Med. J., Norfolk, 9, 1 (1924).
[7] Dutton: "Intravenous Therapy," 398 (1925).

good a coagulating agent, as the things that it displaces. In thus decreasing the degree of agglomeration of the colloids of the dormant plant a stage of stimulation may be reached. Quite obviously not all coagulating agents can fulfill these criteria and cause stimulation. The action of such things as sodium nitrate and sodium thiocyanate is clearly one of peptization thus taking the plant through the stage of stimulation which is observed just before anesthesia and during the recovery period.

Bose[1] studied the effect of various things on *Desmodium*. A dilute alcohol solution acted as a stimulant, whereas the action of a concentrated alcohol solution was that of a depressant. Ether first stimulated the plant; this was followed in succession by depression and narcosis. As would be expected chloroform acted qualitatively like ether. Carbon dioxide acted as a depressant, falling in line with the fact that it acts as an anesthetic[2] for rabbits and dogs. Acid and alkali acted the same way that they do on the mammalian heart.

The literature reveals several interesting things about *Mimosa*. Bose[3] says: "Taking a plant in a subtonic condition, then, we may expect that any application of stimulus will increase its excitability, a fact which will find expression in a growing amplitude of response. This enhancement of excitability will reach a limit at which the plant will be in an optimum condition. After reaching this climax there may be a reversal, with a decline of excitability, a state of things which we associate with fatigue." On page 3 he says: "The most prominent motile organ in *Mimosa* consists of a mass of tissue known as the pulvinus, at the joint or articulation of the primary leaf stalk. The swollen mass on the lower side of this organ is very conspicuous. Under excitation the parenchyma, in this more effective lower half, undergoes 'contraction,' in consequence of which there is a fall of the leaf. This sudden movement constitutes the mechanical response of the leaf to the impinging stimulus, just as the contractile movement of a muscle in similar circumstances forms its characteristic mechanical response." Blackman and Paine[4] report that an excised pulvinus of *Mimosa* when placed in warm water with its internal tissues freely exposed, exhibits, on stimulation, repeated contractions during many hours. This indicates that the loss of turgor in the cells of the lower half of the pulvinus, which is associated with contraction, cannot be explained by a sudden increase of permeability of the tissues allowing a rapid exosmosis of osmotic substances.

Turning again to the work of Bose[5] we find that ozone stimulates *Mimosa*. Carbon dioxide depresses the excitability of the plant, and fresh air restores the plant to normal. Here we have a case of reversible coagulation as the cause of anesthesia. Dilute alcohol vapor sometimes causes a transient increase in excitability; continued application of the vapor causes a depression.

[1] "Researches on Irritability of Plants," 334 (1913).

[2] Leake and Waters: Anesthesia and Analgesia, **8**, 17 (1929).

[3] "Researches on Irritability of Plants," 70 (1913).

[4] Ann. Bot., **32**, 69 (1918).

[5] "Researches on Irritability of Plants," 89 (1913).

Ether depresses the excitability of the plant after an initial short-lived stimulation, producing anesthesia. Carbon disulphide acts in a manner similar to ether. Chloroform acts as a very strong narcotic; the plant exhibits a long recovery period after anesthetization with chloroform.

Wallace[1] made the interesting observation that in the presence of alcohol-free ether vapor,". . . a completely anesthetized *Mimosa* plant is practically identical in appearance with a normal plant for the same time of day. If the plant is exposed to ether during the day, when the leaflets are entirely expanded and the petioles up, the plant remains in exactly this position after anesthetization." He found that he could not anesthetize *Mimosa* in the position that it assumes after stimulation. He found that the leaflets do close up upon anesthetizing with chloroform. "I have obtained closure of some leaflets in concentrations of chloroform as low as 0.1%. I might also say that with the exception of ether, nitrous oxide, ethylene, and acetylene, all of the compounds which I have tested induce a chemonastic reponse similar to that with chloroform.

"Mimosa plants will retain their sensitivity from one to four hours in approximately 100% nitrous oxide and ethylene." The fact that nitrous oxide and acetylene do not behave as narcotics for *Mimosa* under ordinary conditions falls nicely into line with experiments showing that nitrous oxide does not flocculate yeast cultures, and is supposed, along with acetylene to act as an indirect narcotic,[2] having no direct coagulating effect.

Wallace also found that ethyl alcohol is very toxic to *Mimosa*, a concentration of 3% being lethal to the leaflets within ten minutes. "The most interesting characteristic of this alcohol is, however, that the sensitivity of the pulvini increases with increased vapor concentration, apparently to the lethal concentration." He noticed a periodic fall and rise of the petioles under the influence of alcohol.

Experimental Study

1. *Mimosa pudica*, the sensitive plant.

Professor Knudson of the College of Agriculture was good enough to grow a number of *Mimosa* plants for us. We thank him for this and for valuable suggestions in regard to the experiments.

The leaves of a branch were caused to fold up and the petioles fall by means of a mechanical stimulus. The first signs of recovery were manifested in 15 minutes, and the plant was fully recovered in 31 minutes. The temperature of the greenhouse was 21°. A second plant was sprayed with a 5% solution of sodium salicylate. Some of the leaves closed during the spraying process; it was fully recovered in 13 minutes. The plant was sprayed again 32 minutes after the first spraying, and some of the solution was used to water its roots. The sodium salicylate did not appear to be absorbed very readily by the leaves of the plant. A third plant was sprayed with a 1% solution of sodium amytal in order to find out whether or not this anesthetic affects

[1] Am. J. Bot., **18**, 221 (1931).
[2] Bancroft and Richter: J. Phys. Chem., **35**, 254 (1931).

plants. Thirty-two minutes later the plant was again sprayed with the sodium amytal solution. The sodium amytal solution appeared to be more rapidly absorbed than any of the solutions that were used, because under identical conditions the leaves appeared to dry most rapidly. Sodium amytal is apparently not an effective anesthetic for *Mimosa*. A fourth plant was sprayed with a 5% solution of sodium citrate that was just acid to litmus. The plant recovered from the fall due to the mechanical stimulation of the impinging droplets pretty well in nine minutes. It was sprayed again with the same solution after 30 minutes; and some of the solution was used to water it. A fifth plant was sprayed with a 5% solution of sodium thiocyanate; the process was repeated and the plant watered with the solution 29 minutes later. The time of recovery is not important in these experiments because it depends on the degree of sunlight and the experiments were not done simultaneously.

The sensitivity of the treated plants to mechanical stimulus was then tested. The plant that was treated with sodium salicylate was more sensitive in some spots than in others, probably because of an unequal absorption of the salt; white spots of sodium salicylate could be seen on the leaves. This plant seemed to be quite a little less sensitive than an untreated plant, the leaves did not fold up all the way upon stimulating them. The plant that was subjected to the sodium amytal solution responded to stimulation like a normal plant. The plant that was sprayed and watered with sodium thiocyanate was by far the least sensitive to mechanical stimulation; even comparatively powerful blows elicited only a faint folding response on the part of the leaves; and the petioles dropped only slightly. The plant that was treated with sodium citrate was more sensitive than any of the other treated plants.

A test was made upon the rate of recovery from a mechanical stimulus sufficiently powerful to drop the primary petioles and cause the leaves to fold. The plant treated with sodium thiocyanate was not included because so violent a shock was necessary to cause a dropping of the petioles that the plant was actually anesthetized, although it turned out to be as slow as the sodium salicylate plant in recovering. Thirty-nine minutes after the start of the experiment the treated plants had recovered in the following order from most to least: sodium amytal > sodium citrate > control > sodium salicylate. At the same time the order of sensitivity of the plants as nearly as could be determined was: sodium thiocyanate < sodium salicylate < control > sodium citrate > sodium amytal. At first sight it appears that there is no rhyme or reason to these results, but closer inspection reveals much. The symptomatology of coagulation and of over-peptization may quite reasonably be the same. Consider a collodion bag, closed at both ends and filled to 85% of its capacity with egg white containing 10% of ammonium sulphate. Now, if one immerses this contraption in distilled water it will fill to the breaking point by osmosis and become more resistant to bending than it formerly was, it being against the rules to break the bag. Likewise, if one immerses the system in boiling water the albumin will coagulate to a hard mass thus also making the bag unbendable. Qualitatively the same outward result, then, has been achieved both by coagulation and peptization. In the sensitivity series we have sodium

thiocyanate and sodium salicylate acting as peptizing agents; while sodium amytal and sodium citrate are acting as coagulating agents. As one would expect, sodium amytal is a better coagulating agent than sodium citrate. At the same time they all produce the same symptoms. The recovery series can be taken as a comparison of the state of excitability of the individual plants. The least recovered plants, those treated with sodium salicylate and sodium thiocyanate, were quite obviously in the state of least excitement; those treated with sodium amytal and sodium citrate were in the most excited condition. If these data are regarded as accurate enough, the sensitive plant falls into line beautifully with the reversible coagulation theory of anesthesia.

From the behavior of the plants treated with sodium thiocyanate and sodium salicylate it would appear that the peptization phenomenon in these cases is intimately concerned with the imbibition of water. Cytolysis is, therefore, probably the cause of death by toxic doses of sodium thiocyanate.

A 16-liter bell jar was inverted over a healthy sensitive plant, a wad of cotton on which was poured five cc. of ether, containing about 0.3% of alcohol as impurity, was placed beside the pot. The bell jar was then sealed to a glass plate. After 38 minutes the plant did not appear to be anesthetized. When removed at this time neither the pulvinus nor the leaves had lost their sensitivity; on the contrary, they appeared to be more sensitive than they normally would be. The plant was probably in the stage of excitation. The process was repeated using another plant and three times the amount of ether was used. This plant was not completely anesthetized in one hour 36 minutes. The sensitivity of the leaves to mechanical stimuli was gone for they did not close upon being touched; but the pulvinus was extremely sensitive, because the petioles fell upon very mild mechanical stimulation. This is in accord with the finding of Wallace[1] that at higher temperatures the pulvini often remained sensitive after the leaflets and part of the primary petiole were entirely dead and dried up. At the same time that this plant was confined to the bell jar there stood beside it a plant that had been treated previously by twice spraying it with a 5% sodium thiocyanate solution. When removed from the anesthetizing chamber after one hour 36 minutes neither the pulvinus nor the leaves were sensitive to mechanical stimulation; the leaves were not closed and the petioles did not fall. That this is truly a case of antagonism between ether, a coagulating agent, and sodium thiocyanate, a peptizing agent, will be more evident in the light of the experiments that will be described next.

Five cc. of ether were poured on the soil in which a potted sensitive plant was growing without touching the plant. One leaf closed up and the petiole fell immediately. Complete anesthesia ensued in four minutes; both the leaves and the petioles were affected so that the plant was completely folded up. The sensitivity of the pulvini began to return several times as was evidenced by an extremely slight rise of the petioles, but each time they fell again. After one hour the pulvini were slightly sensitive and the petioles had risen

[1] Am. J. Bot., 18, 293 (1931).

a few millimeters; the leaves had not opened at all. At the same time a plant that had been sprayed twice with a 5% solution of sodium thiocyanate, and had stood for about 30 minutes after the second spraying, was treated by pouring five cc. of ether on the soil, being careful not to touch the plant. After six minutes the anesthetic had a slight effect; the leaves were not affected at all so far as one could see, for they did not close. In the case of the control plant the petioles dropped until they were supported by the edge of the pot; whereas in the case of the plant treated with sodium thiocyanate the petioles dropped about one quarter as far and were fully erect again 17 minutes after they fell.

Another plant was anesthetized by pouring five cc. of ether on the soil. It took five and one-half minutes for the ether to take effect, at which time the petioles fell and the leaves closed. After 40 minutes the pulvini were slightly sensitive as evidenced by a few millimeters rise of the petioles and by their dropping again when touched. Five cc. of ether was carefully poured on the soil of still another plant at the same time that the above plant was so treated. The leaves closed and the petioles fell in two and one-half minutes. A minute and one-half later the plant was sprayed with a 5% solution of sodium thiocyanate. Eighteen minutes later the leaves were partly open; the petioles were partly raised; and the pulvini were quite sensitive.

Thus it has been shown that it is possible to reduce markedly the narcotic action of the coagulating agent ether upon the sensitive plant by employing the well-known and efficacious peptizing agent, sodium thiocyanate. Likewise, as the theory demands, sodium thiocyanate aids materially in the recovery of *Mimosa* from anesthesia.

2. *Lycopersicon lycopersicum*, the tomato plant.

Crocker[1] reports that "a vigorously growing tomato plant will have its leaves turned back to a noticeable degree by concentrations of illuminating gas (with 9 to 10% illuminants) as low as one part of gas in 100,000 to 200,000 of atmosphere." Ethylene was found to be the constituent mainly responsible for the effect. "The response of the tomato plant to gas is a growth response. . . ."

A paper by Crocker and Knight[2] contains the following summary: "The flowers of the carnation are extremely sensitive to traces of illuminating gas in the air.

"With the Boston Market and Pink Lawson three days exposure to 1 part in 40,000 kills the young buds and prevents the opening of those already showing the petals. The buds of medium age are considerably more resistant.

"In the same varieties 1 part in 80,000 causes the closing of the open flowers upon twelve hours' exposure.

"This injury takes place directly on the bud or flower exposed and not indirectly through absorption by the roots.

"The 'sleep' of the carnation is probably often caused by traces of illuminating gas in the air.

[1] Florists Exchange and Horticultural Trade World, **70**, 15, 54 (1929).
[2] Bot. Gaz., **46**, 259 (1908).

"Ethylene is even more fatal to the flowers of the carnation.

"Twelve hours exposure to 1 part in 2,000,000 causes the closing of flowers already open."

Ethylene also causes the leaves of *Mimosa* to drop, which means that in that case also it acts as an anesthetic.

With these things in mind attempts were made to apply the reversible coagulation theory of anesthesia to tomato plants after they had been acted upon by ether in one case, and by ethylene in another case. Two young, recently potted, tomato plants were placed in a 14 liter bell jar which was maintained at 26°, to within one degree by means of an electric light above the jar. Ten cc. of ether, in an evaporating dish, were placed in the bell jar which was then sealed to a glass plate. The experiment was started at 9:35 a.m. At 5 p.m. the only noticeable effect of the ether on the plant was a slight drooping of the leaves and petioles. Ten cc. more ether was placed in the evaporating dish at this time.

At 12:15 a.m. both plants were drooping and limp, so they were removed from the anesthetizing chamber. One plant appeared to be in a little poorer condition than the other; this plant was sprayed immediately with a 5% solution of sodium thiocyanate, and watered with 15 cc. of the solution at the same time. The other plant was sprayed with tap water and watered with 15 cc. of the same. The plants gave off quite a little water while in the bell jar. Forty-five minutes after the plants were watered and sprayed they were in bad shape. At this time the plant treated with water did not appear to droop so much and was not so limp as the one treated with sodium thiocyanate. It was noticed that the leaves of the control plant tended to curl up laterally; whereas the leaves of the plant treated with sodium thiocyanate exhibited no such tendency. Also, the control plant appeared to be more withered than the other. An hour and one-half after the plants were removed from the anesthetizing chamber and treated, the control plant appeared to be in much worse general condition than the one treated with sodium thiocyanate.

At 10:00 a.m., or a little more than 24 hours after the start of the experiment the leaves of the control plant were shrivelled, dry, and crisp; the leaves of the other plant were shrivelled but neither dry nor crisp. This same condition of affairs persisted for at least three more days. The stem and petioles of the plant treated with sodium thiocyanate apparently shrank a great deal. This observation gave rise to the suggestion that perhaps the tomato plant is impermeable to the thiocyanate ion. A qualitative test for the ion was strongly positive indicating that the plant is probably permeable to it.

The next experiment was performed using ethylene as the anesthetic. Two tomato plants were placed under a 16 liter bell jar containing 25 cc. of ethylene at 6:00 p.m.; at 10:40 p.m. the plants did not seem to have responded to the anesthetic so the bell jar was aired out and 50 cc. of ethylene put into it. At 12:15 a.m. the primary petioles of both plants were curled up so that the far tips of the leaves touched the main stems. The appearance of the primary petioles was the same as described by Crocker[1] for all of the petioles of a

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[1] Florists Exchange and Horticultural Trade World, **70**, 15, 54 (1929).

vigorous young plant. One plant appeared to be a little bit more affected by the ethylene than the other.

At 12:15 a.m. the plant that was in the worse condition was sprayed with a 5% solution of sodium thiocyanate and watered with 15 cc. of the solution. The other plant was treated in exactly the same manner, only tap water was used instead of sodium thiocyanate solution. Forty-five minutes later the primary petioles and leaves of the control plant were in exactly the same position as they were at the time the plant was sprayed. The leaves and petioles were perhaps a little more stiff and resistant to touch than those of an untreated plant. The plant that was treated with sodium thiocyanate presented an entirely different picture. The leaves and petioles were drooping and limp. The leaves of the control plant were erect on the petioles and the petioles were bowed.

The control plant still showed very markedly the effect of the anesthetic 24 hours after it was removed from the atmosphere containing ethylene. At this time the plant treated with sodium thiocyanate was in very bad condition; all of the petioles had fallen and the leaves were shrivelled, but they were not dry. Although the sodium thiocyanate was apparently toxic to the plant the leaves had not dried out even after three days. It was found in a later experiment that a 1% sodium thiocyanate solution is slightly toxic to the tomato plant.

It is important to note that the sodium thiocyanate acted upon the primary petioles, which were the ones most affected by ethylene, within 45 minutes; whereas, it took quite a few hours for the other petioles to respond to the sodium thiocyanate.

These experiments show that the death of the tomato plant from an overdose of ether is retarded by sodium thiocyanate, as it should be if the theory of reversible coagulation holds. Likewise, as one would predict, the stimulation brought about by ethylene is counteracted by sodium thiocyanate.

The effect of sodium thiocyanate may be produced in either or both of two ways. In the first place it may peptize the colloidal system of the plant directly. Since we know of no protein that is not peptized by sodium thiocyanate, it seems that this mechanism must always be a part of the picture. Also, the sodium thiocyanate may alter profoundly the capacity of the plant cells to imbibe water, in the direction of greater imbibition. This seems to be the preponderant action in the case of the sensitive plant. That sodium thiocyanate repeptizes the reversibly coagulated colloids of a plant affected by an anesthetic seems certain, and is as it should be. Here again it is important that the amount of coagulation induced by an anesthetic may be so small as to go unnoticed even under the ultramicroscope. The same thing holds for the peptization of the plants colloids *in vivo*.

The general conclusions supported by this paper are as follows:

1. In animals and plants the effect of an anesthetic upon the bio-colloids is that of reversible coagulation.

2. Ether, chloroform, alcohol, distilled water, magnesium sulphate, carbon dioxide, ethylene, heat, and cold have been found to anesthetize a variety of plants by various workers.

3. Plants respond in a manner similar to animals to electrical stimulation. Fatigue and various irritability phenomena occur alike in plants and animals.

4. Anesthetics produce in plants a preliminary stage of excitation, as they should.

5. Protein coagulation is the cause of the depression of plants by heat.

6. The term reversible gelation is applied by Nichols to the effect of chloroform on Nitella.

7. The colloids from macerated wheat sprouts are flocculated by many cations, the lyotropic series being the same as that for egg albumin. Likewise, there are ion antagonisms of the same sort as are found in animals.

8. The effects of sodium thiocyanate, sodium salicylate, sodium citrate, sodium amytal, and ether on plants are exactly as the theory of reversible coagulation demands; the first two peptize the bio-colloids, and the last three coagulate them.

9. Anesthesia of the sensitive plant by ether has been antagonized by sodium thiocyanate by employing the salt before the anesthetic and after the anesthetic.

10. Sodium thiocyanate causes *Mimosa* to become rigid, due probably to the imbibition of water by the colloids of the plant.

11. The death of the tomato plant as a result of over-exposure to ether is greatly retarded by sodium thiocyanate.

12. Sodium thiocyanate has, as one would expect, a more rapid action upon those leaves of the tomato plant that are most affected by ethylene.

13. The effect of ethylene upon the tomato plant appears to be counteracted by sodium thiocyanate.

14. The action of ethylene upon the tomato plant is one of stimulation which means in the terms of this theory partial coagulation of the bio-colloids. Sodium thiocyanate appears to repeptize these colloids.

15. Sodium thiocyanate breaks the dormant period of potato tubers. This is exactly what should happen if the colloids of the dormant tubers are somewhat agglomerated.

16. Claude Bernard's theory of anesthesia as developed in the laboratories of the senior author applies without modification to plants.

Cornell University.

COLLOIDAL PHENOMENA IN GALL STONES

BY HARRY B. WEISER AND GEORGE R. GRAY

The importance of colloidal behavior in the formation of gall stones and other concretions has been recognized for a long time. Thus Hippocrates and Galen, the fathers of medicine, attributed such formations to an accumulation of mucus which clung to the organ and served as a nucleus for the stone which subsequently formed. The first experimental evidence which indicated the rôle of colloids in concrement formation was obtained by A. von Heyde who dissolved out the crystalline material from urinary calculi and observed a residual framework. This was recognized quite clearly by Meckel von Helmbach in his book on Microgeologie published in 1856. Thus he writes: "Two basic factors underlie the formation of every true gall or urinary stone; first, the presence of an organic substance, mucus, in which there may be deposition of salts; second, a suitable urinary or gall fluid to serve as the mother liquor for these sediments. The decomposable organic substance, mucus, is unquestionably necessary, because urinary salts and gall substances of themselves can yield only crystalline, pulverulent or granular precipitates and never larger pieces. Stones are formed only when an organic binder is carried down too."

While the presence of an organic binder resulting from inflammatory processes has been definitely established as essential for the formation of certain types of gall and urinary stones,[1] it was demonstrated twenty years ago by Aschoff[2] and by Schade[3] that both gall and urinary calculi may form under certain conditions without being accompanied by inflammation. In this paper the colloidal phenomena which are concerned with the formation of gall stones without coexisting inflammation will first be reviewed, after which gall stones formed during inflammation will be considered especially from the point of view of the mechanism of the formation of the concentric rings or layers in such stones.

Gall Stones formed without Inflammation

When stones are formed in the gall bladder without the coexistence of inflammation there is usually but a single stone composed largely of cholesterol. Such stones are called "pure cholesterol stones" although they usually

[1] Pfeiffer: 5th Cong. Int. Med., Wiesbaden (1886); Posner: Arch. klin. Med., **5**, (1885); **16**, (1889); Naunyn: "Klinik der Cholelithiasis," Leipzig (1892); Gilbert and Dominici: Compt. rend. soc. biol., **28**, 1033 (1893); Moritz: 14th Cong. Int. Med., Wiesbaden (1896); Gilbert: Arch. gén. de Méd., **2**, 257 (1898); Gilbert and Fournier: Presse Med., **7**, 259 (1898); Mignot: Arch. gén. de Méd., **2**, 129, 263 (1898); Schreiber: Virchow's Archiv, **153**, 147 (1898); Cushing: Bull. Johns Hopkins Hosp., **10**, 166 (1899).

[2] Aschoff and Bacmeister: "Cholelithiasis" (1909); Kleinschmidt: "Die Harnsteine" (1911).

[3] Münch. med. Wochenschr., Nos. 1 and 2 (1909); Kolloid-Z., **4**, 175, 26 (1909); Kolloid-chem. Beihefte, **1**, 371 (1910); Alexander's "Colloid Chemistry," **2**, 801 (1928); cf., also, Boysen: "Uber die Struktur and Pathogenese der Gallensteine" (1909).

contain small amounts of alkali and calcium cholates, bile pigments, etc. Fig. 1 shows a cross section of a stone which is nearly pure cholesterol. The specimen is white, hence is free from bile pigments. A portion of the stone was found to be almost completely soluble in ether, which indicates the absence of alkali or calcium cholates.

A probable mechanism of the formation of such "pure cholesterol stones" was suggested by Ord[1] and was extended and formulated by Schade.[2] The
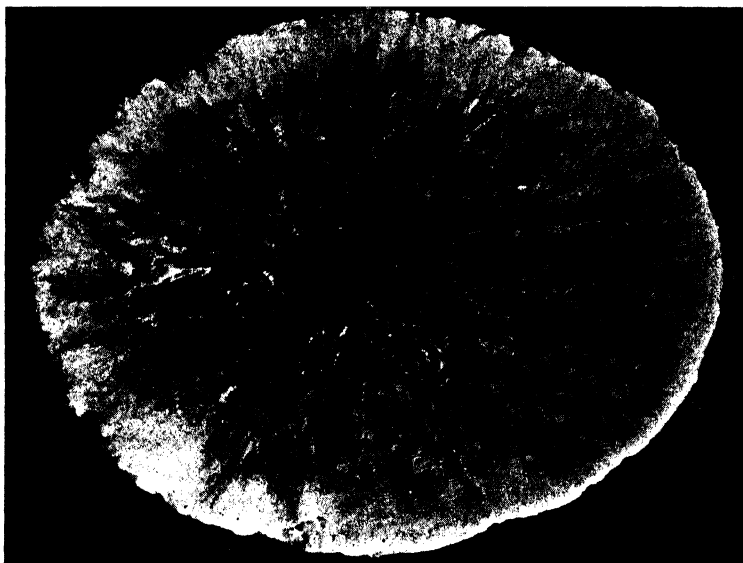
Fig. 1
Cross-Section of Pure Cholesterol Stone. ($\times$ 6)

latter demonstrated that when a 2 to 6 per cent solution of cholate is saturated with cholesterol at approximately 80° and the solution cooled rapidly, a cloud of formless white flocs of cholesterol separates out; if the cooling is quite slow relatively large crystals are obtained. On the other hand, if the hot cholate-cholesterol solution is shaken with a drop of olive oil, gall fat, or petroleum oil, and then cooled, the cholesterol separates in myelin-like drops with the oil phase. These drops, which at first are transparent soft bodies, coalesce and undergo crystallization with the separation of fat, giving radially crystal-line spheres of almost pure cholesterol.

A similar phenomenon apparently takes place in stasis of the bile. This secretion which at first possesses a slight alkaline reaction consists of a mixture of alkali cholates, bile pigments, cholesterin, lecithin, fats and soaps, as well as electrolytes which are widely distributed in the body fluids. The cholesterol is colloidally dispersed in the bile fluid by the protective action of the alkali cholates. Now in stasis of the bile, it has been demonstrated by the surgeon

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[1] "The Influence of Colloids on Crystalline Form and Cohesion" (1879).

[2] Kolloidchem. Beihefte, 1, 375 (1910).

and pathologist that the amount of cholates diminishes gradually owing to resorption and autolysis, leaving a fluid which may be clear and almost cholate free. This gradual disappearance of cholates leaves a supersaturated solution of cholesterol which separates out.[1] But owing to the presence of fat and soaps in the fluid, the separation is in the form of drops which coalesce and subsequently crystallize initiating "pure cholesterol" gall stones.

From the above it would appear that stasis of the bile may in itself lead to the formation of gall stones especially if there is an impairment of liver function giving a bile deficient in cholates. It is probable that there are other contributing causes not associated with inflammation, which favor the separation of the cholesterol, in such a condition that stones result. Thus Thudichum[2] points out that a stagnant and infected bile will decompose giving an acid reaction. This would convert the cholates into insoluble cholic acids which would allow the cholesterol to precipitate. In this connection Wrada,[3] Neilson and Meyer[4] and Rous, McMaster and Drury[5] found that bile taken from the gall bladder was slightly acid in a large proportion of cases while that taken from the hepatic duct was nearly always somewhat alkaline and usually markedly so. Whatever may be the cause of the normal change in pH in the gall bladder, it occurred to Petersen[6] and Miller that gall stones might be formed by altering definitely the pH value of the bile. A distinctly acid bile was obtained in a number of experimental animals by grafting a pedicled flap of the stomach to the gall bladder wall and an alkaline bile by anastomosis of the gall bladder to a portion of the duodenum. The bile from gall bladders containing the duodenal transplants was regularly alkaline and was more viscid than normal bile; but no evidence of stone formation was observed in six months. The gall bladders having the gastric transplants always yielded an acid bile. No definite concretions were obtained but the gall bladder wall appeared reddened and congested, with cholesterin particles scattered over the entire surface. This condition is what is known clinically as "strawberry gall bladder," recognized as a forerunner of gall stones.

These observations of Petersen disprove the contention of Porges[7] that free, unneutralized acid will not remain in contact with the mucous membrane of the gall bladder and the claim of Bacmeister[8] that the addition of small amounts of acid to the bile is unsuitable for bringing about the precipitation of cholesterol.

The hypothesis that the destruction of cholates by bacterial action contributes to the formation of gall stones as claimed by Exner and Heirovosky[9] and Bondi and Hess[10] on the basis of observations in vitro, is open to the

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[1] Cf. Oliver: J. Lab. Clin. Med., **8**, 242 (1923).

[2] Virchow's Archiv, **156**, 384 (1899).

[3] J. Physiol., **50**, 114 (1915).

[4] J. Infect. Dis., **28**, 511 (1921).

[5] J. Exp. Medicine, **39**, (1) 77; (2) 97; (3) 403 (1924).

[6] Unpublished paper.

[7] Kolloid-Z., **5**, 301 (1909).

[8] Münch. med. Wochenschr., Nos. 5, 6, and 7 (1908).

[9] Arch. klin. Chu., **86**, 609, 643 (1908).

[10] Wiener klin. Wochenschr., **21**, 271 (1908).

objection that even under the extreme conditions chosen by them, there still remained enough cholates to keep the cholesterol dispersed.[1]

As a result of chemical-pathological investigations, Chauffard[2] observed that stone formation in the absence of inflammation is frequently accompanied by a pathological condition which results in an increase in the cholesterol content of the blood. In such cases the primary cause is a disturbance in the metabolism.

Since cholesterol is colloidally dispersed in the bile, Porges[3] attempts to explain the precipitation by assuming the coagulating action of substances on the sol. His suggestion follows from analogy with the behavior of hydrosols of lecithin and cholesterol toward electrolytes. The difficulty is that one must postulate the presence in the bile of an amount of coagulating electrolyte considerably larger than is likely to be present.

While all of the above factors may contribute to the formation of gall stones in the absence of inflammation, it seems probable that sufficiently marked stasis of the bile to allow of resorption of the cholates is adequate in itself to cause stone formation provided the conditions are favorable for the separation of the cholesterol in myelin-like drops which coalesce and subsequently undergo crystallization. This would seem to be particularly true if the bile were deficient in cholates or especially rich in cholesterol as a result of impaired liver function.

In addition to the pure cholesterol stones, pure pigment stones[4] and pure calcium carbonate stones[5] are formed under certain conditions without apparent inflammation. Peel[6] analyzed some pigment stones of this kind and found them to be entirely free from cholesterol. They contained some free pigment but were largely calcium and copper bilirubinate. The following description of these stones indicates that like pure cholesterol stones, they are formed as a result of the dropwise separation of the insoluble calcium salts of the bile pigments: "They vary in size from that of a pin-head to a cherry seed and possess a fine granular surface such that they appear as if they were built up of several small globules. In a fresh condition they are somewhat hard; on drying, the hardness increases enormously. In cross section they appear uniform throughout. They show neither radial nor concentric layers nor a distinguishable central core."

The formation of the pure calcium pigment stones is probably favored by a disturbed metabolism which gives a bile relatively rich in pigments and in calcium and possibly copper salts.[7] It is probably true that this condition alone without inflammation would not cause the calcium pigment to precipitate as a concrement unless the initial separation was in the form of drops.

[1] Porges: Kolloid-Z., 5, 301 (1909).

[2] Leçons sur le lithiase biliare" (1914).

[3] Kolloid-Z., 5, 301 (1909); Porges and Neubauer: Biochem. Z., 7, 152 (1907).

[4] Boysen: Uber die Struktur und Pathogenese der Gallensteine" (1909; Bacmeister: Ergebn. inn. Med., 11, 1 (1913).

[5] Halpert: Arch. Path., 6, 630 (1928).

[6] Z. physiol. Chem., 167, 269 (1927).

[7] Peel: Z. physiol. Chem., 167, 274 (1927).

Gall Stones of Inflammatory Origin

An inflammation in the bile ducts or the gall bladder introduces into the bile irreversibly precipitating hydrophilic colloids such as serum albumin, globulin, and fibrin.   If cholesterol or calcium bile pigments separate in the presence of such colloids, there is mutual adsorption with the result that the whole is united into a coherent mass giving what is sometimes termed a colloid-crystalline stone as distinct from the pure crystalline stone considered in the last section.   Since gall stones are usually of inflammatory origin, it follows that colloid-crystalline stones are the type most commonly found in the gall bladder.

As has been pointed out, the formation of stones in the absence of inflammation is probably preceded by the separation of the stone-forming material in a drop-like form.   A similar condition may obtain when inflammation is present but in the latter case dropwise separation is not essential since the colloidal material resulting from the inflammatory process may bind the mass firmly into a concrement.   Indeed, Schade[1] produced stones artificially by allowing coagulation of fibrin to occur in solution in which freshly precipitated, sediment-like discrete crystals were suspended.

The importance of the colloidal binding material in concrement formation is shown by dissolving out first one constituent and then the other from a colloid-crystalline stone.   If the crystalline material is removed with a suitable solvent, a firm coherent skeleton of colloidal matter remains which shows the details of structure of the stone.   On the other hand, if the albuminous skeleton is dissolved out by antiformin, there is complete disintegration, nothing remaining but a slimy mass of minute crystals.[2]

Since the relative amounts of the various constituents which make up gall stones of inflammatory origin may vary widely, it is obvious that the composition, appearance, and physical properties of the stone will show almost infinite variation.   In a stone in which there is a relatively small amount of hydrophilic colloid, the soft irregular masses consisting largely of cholesterol, undergo solution and recrystallization, ultimately giving a radial structure similar to that in the pure cholesterol stone.   Adsorption of the bile pigments or their precipitation as the calcium salt[3] stains the stone to a greater or lesser degree depending on the relative amount of pigment adsorbed or thrown down.   If the amount of hydrophilic colloids present in the stone is relatively large, crystal growth is inhibited and the formation of long crystals is prevented.   Since the hydrophilic colloids lose water and shrink with time, stones containing a large amount of such colloids may become sufficiently friable that they fall to pieces.   In other cases the ageing may make radial rifts leading out from the center leaving an irregular hollow space which fills with liquid.

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[1] Münch. med. Wochenschr., Nos. 1 and 2 (1909).

[2] Schade: Med. Klinik, No. 15 (1911).

[3] The so-called calcium salt of the bile pigments is probably an adsorption complex of indefinite composition.

The most common form of gall stones are the colloid-cholesterol-calcium pigment stones that are characterized by the presence of concentric rings varying in color. Such concretions are termed layered stones or "common gall stones." In these stones the kernel and the surrounding ring structure are readily distinguished. The former consists largely of albumin, calcium, bilirubin and cholesterol without the presence of a definite ring structure while in the latter, there are a number of colored rings in crystals of cholesterol.

Gall stones of inflammatory origin seldom or never occur singly. In rare instances there may be but two or three stones but, as a rule, there is a much larger number, 100 or more in some cases. Because of the pressure of the gall bladder the stones are seldom spherical but are faceted and usually of widely varying shapes. In certain cases the shape may be more or less uniform. In a collection obtained from one gall bladder there were 50 stones each of which was an almost perfect pyramid with rounded edges.

The cause of the concentric rings in the common gall stones is usually attributed to layering as a result of variations in conditions which produce alternate layers of cholesterol and pigment. Schade[1] attributes the formation of a layered rather than a radiating structure to the effect of pressure which flattens out the crystals of cholesterol. This does not account for the beautiful regular formation of alternate dark and light rings. Moreover, in most stones of this type there is a distinct evidence of radiating structure and in many cases this is quite marked as shown in the photographs of the cross-section of stones shown in Figs. 2 and 3.

The appearance of the concentric rings suggests to the colloid chemist that they may originate as a result of the rhythmic banding first described by Liesegang as a result of his observations of the formation of rings of silver chromate when silver nitrate is allowed to diffuse into a gelatin jelly containing dichromate. The possibility that the rings in gall stones are not layers but rhythmic bands has been taken seriously by few people. Schade[2] dismisses the suggestion promptly by contending that for the formation of Liesegang rings as a primary process, the diffusion must take place in a jelly which has no points of resistance to diffusion. This, he points out, does not obtain in gall stones owing to the presence of crystalline cholesterol irregularly included in the framework of hydrophilic colloids. Moreover, he rules out the formation of Liesegang rings as a secondary process, since this would give very irregular lines, which do not occur.

Sweet[3] takes the position that the concentric rings are due to the Liesegang phenomenon. He gets around the difficulty confronting Schade by postulating that the cholesterol forms a gel containing calcium into which the bile pigments such as bilirubin can diffuse giving rhythmic bands of calcium bilirubin just as silver nitrate diffuses into dichromate-gelatin jelly and gives rhythmic bands of silver chromate.

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[1] Alexander's "Colloid Chemistry," 2, 817 (1928).

[2] Alexander's "Colloid Chemistry," 2, 830 (1928).

[3] Colloid Symposium Annual, 8, 249 (1930).
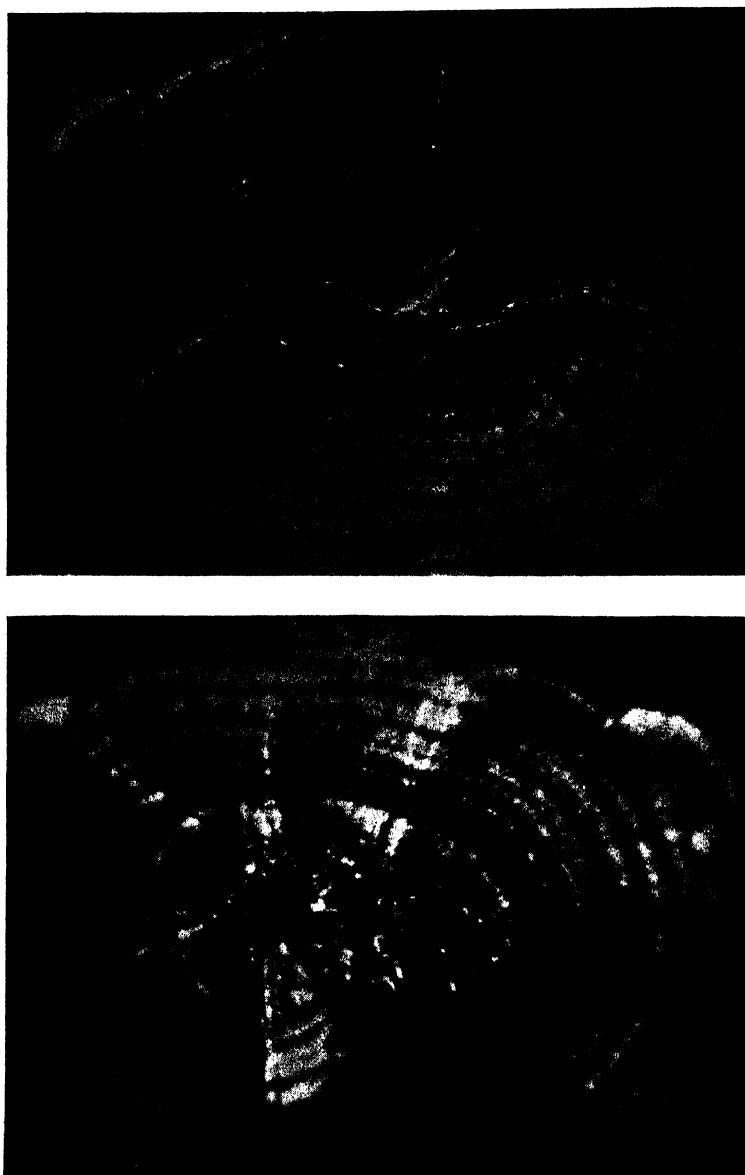
FIG. 2

Cross-Section of Natural Gall Stones showing both Ring and Radiating Structures. ($\times$ 10).
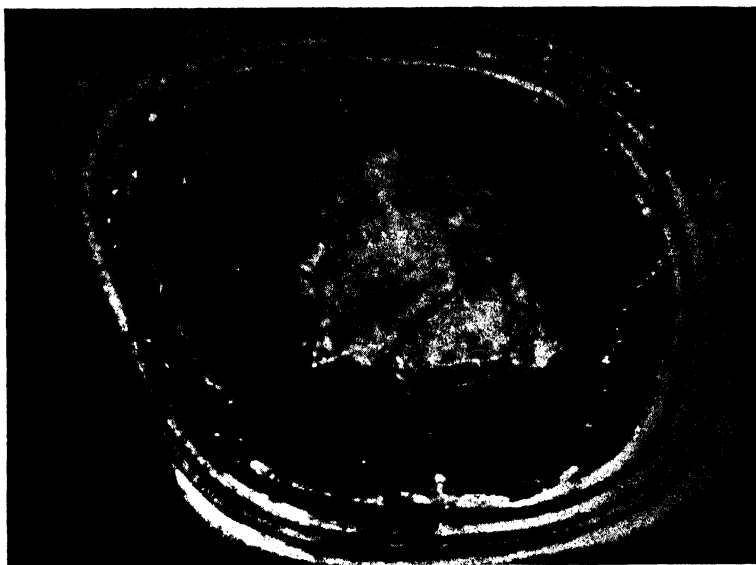
FIG. 3
Cross-Section of Natural Gall Stone. ($\times$ 10).

A consideration of the gall stone-bile system reveals, however, a marked difference between it and the gelatin-electrolyte system of Liesegang. In the first place, the gall stone is probably not a true jelly at any stage of its history, as assumed by Sweet. And if it did possess a true jelly structure like that of gelatin, rhythmic bands could not form as a result of diffusion since the bile pigments are in colloidal solution and so diffuse but little if at all. Schade's objection to the banding theory on the ground that rhythmic precipitation takes place only in a jelly, does not hold since the phenomenon manifests itself not only by diffusion into jellies but also into relatively non-uniform amorphous and crystalline masses. Accordingly, it is altogether possible that the precipitation of crystalline cholesterol in the presence of hydrophilic colloids will, under certain conditions, give a mass into which the colloidal pigment can diffuse and by interacting with lime or other calcium salt carried down with the cholesterol, precipitate colored rhythmic bands. In other words, the very fact that cholesterol is definitely crystalline may be the determining factor in producing rhythmic bands therein since a mass of small crystals would allow the interdiffusion of the colloidal bile pigments.

If this is a true statement of the case it should be possible to simulate the conditions sufficiently closely that rhythmic bands of calcium bile pigment will be formed in a mass of precipitated cholesterol containing lime. This has actually been accomplished as will be described in the following experiments.

Experimental

Rhythmic Bands of Ag_2CrO_4 in Cholesterol. To show that rhythmic banding will take place in a mass of cholesterol crystals, the following experiments were carried out: One gram of gelatin was dissolved in 100 cc. of water con-

taining 0.1 gram of K_2CrO_4 and heated to 70°. Into this solution was poured rapidly 25 cc. of a hot alcoholic solution of cholesterol containing 2 grams of the pure compound. The cholesterol precipitated immediately in the form of minute crystals. These were matted firmly and uniformly in the bottom of a test tube by centrifuging and the supernatant solution was poured off. The precipitate was then covered with an 8 percent solution of $AgNO_3$. Upon standing, the familiar rhythmic bands of Ag_2CrO_4 were formed.

The above procedure was repeated keeping all the factors constant except the amount of gelatin in the solution into which the alcoholic cholesterol was poured. The gelatin solutions contained 0.75, 0.50, 0.25 and 0.05 gram, respectively, in 100 cc. In every case rhythmic bands were formed. With decreasing amounts of gelatin the bands were broader, less distinct and further apart. When no gelatin was used, bands were not formed, but crystals of Ag_2CrO_4 were scattered irregularly throughout the mass.

Portions of the precipitate thrown down in the presence of a small amount of gelatin when placed on a watch glass and surrounded with silver nitrate gave rhythmic rings similar to those obtained by diffusion in gelatin.

Since bands of silver chromate in cholesterol are formed in the presence of such minute amounts of gelatin, it is obvious that the rhythmic precipitation is not taking place in a gelatin jelly. The gelatin merely serves to inhibit the growth of the cholesterol crystals and so to give a mass of minute crystals in which the diffusion phenomenon can take place under such conditions that rhythmic bands or rings result.

Rhythmic Bands of Calcium Bile Pigment in Cholesterol. Solutions of bile pigment were prepared in the following way. Twenty-five grams of finely powdered human gall stones were extracted in a Soxhlet tube with 200 cc. of ether for two days to remove cholesterol and fat. The residue was dried, washed with hot water, then with 10 percent acetic acid and finally with water. This residue was dried and ground in small portions with 2 N NaOH and the filtered solution was used in the experiments. When a portion of the highly colored solution was subjected to dialysis in a cellophane bag, the color did not diffuse showing that it was in the colloidal state just as it is in the bile fluid. The addition of a dilute solution of calcium nitrate did not result in immediate precipitation of the calcium-pigment complex but upon standing, a precipitate settled out which varied in color from reddish brown to olive green, depending upon the degree of oxidation of the pigment.

Although the colloidal bile pigments do not diffuse through gelatinous membranes, it seemed not unlikely, in the light of the above experiments with Ag_2CrO_4, that a suitably precipitated mass of cholesterol crystals containing calcium would serve as a medium into which the colloidal pigments would diffuse to form rhythmic bands, thus simulating the process which probably takes place in nature. This hypothesis was confirmed by the following method of procedure: Into 50 cc. of a solution containing 0.5 gram of gelatin and 0.5 gram of calcium nitrate at 70° was poured 12.5 cc. of a hot alcoholic solution of cholesterol containing 1 gram of the pure compound. After prolonged centrifuging the supernatant solution was removed from the mass of precipitate and
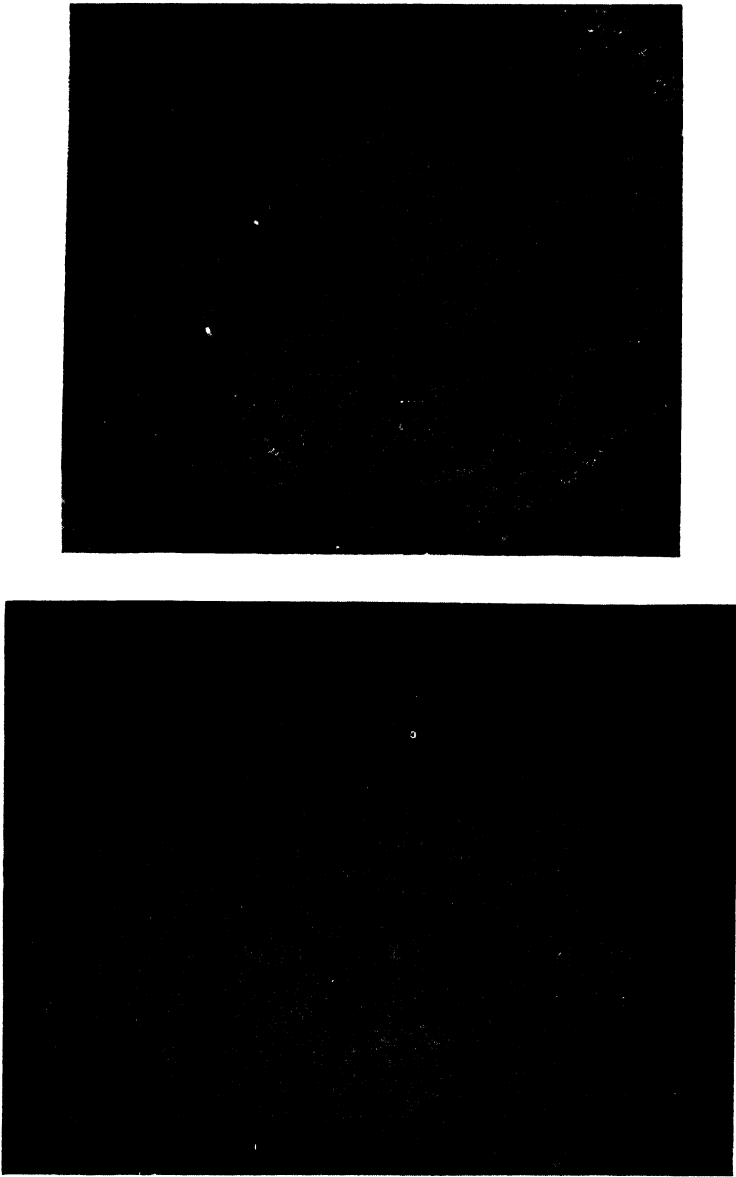
FIG. 4
Synthetic Cholesterol-Calcium Pigment.
Gall Stones showing Rhythmic Banding. ($\times$ 10).
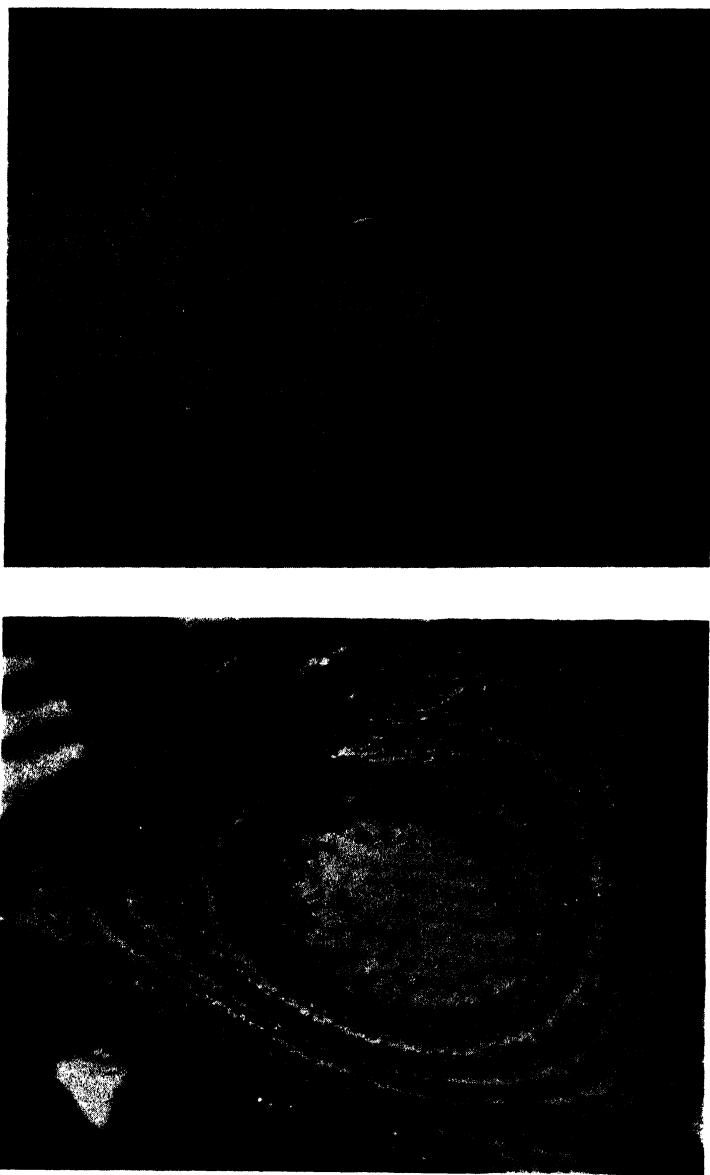
FIG. 5

Synthetic Cholesterol-Calcium Pigment Stones showing how the Shape of the Stone influences the Form of the Rhythmic Bands. ($\times$ 10).
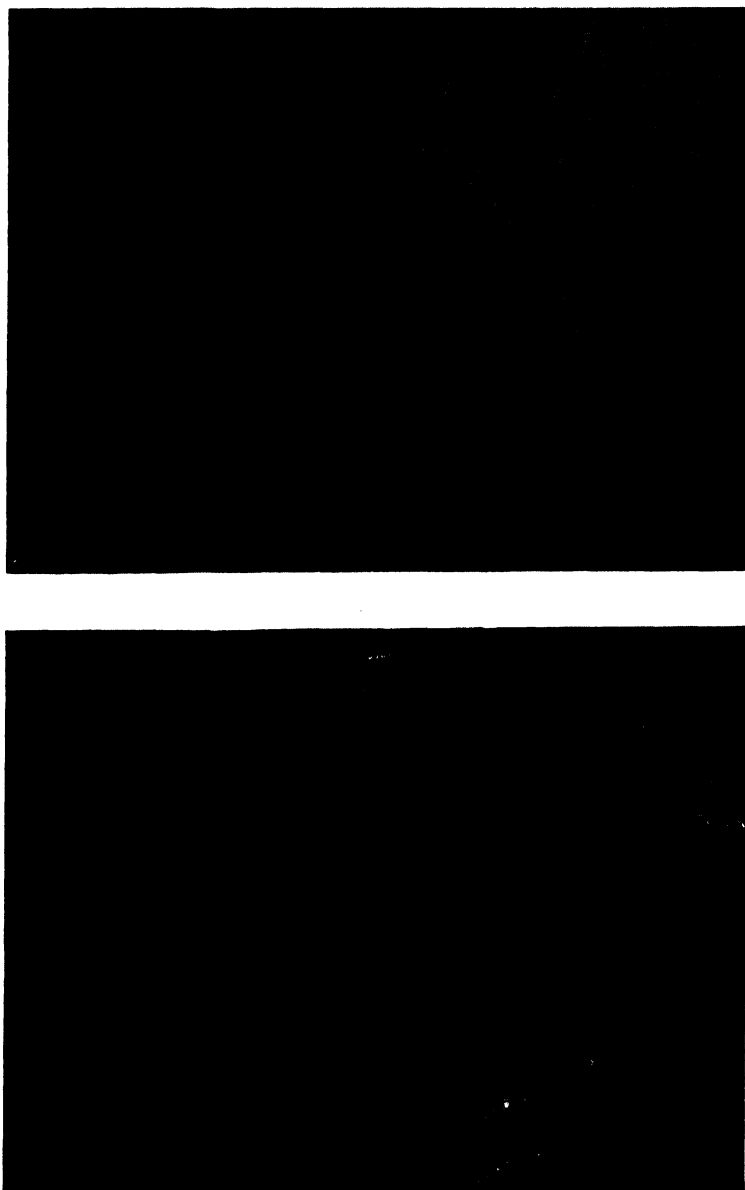
FIG. 6

Synthetic Cholesterol-Calcium Pigment. Gall Stones formed in the presence of a Small Amount of Fibrin.

portions of the latter were placed on a microscope slide and surrounded by the solution of bile pigments. The specimens were placed in a desiccator containing an ammonia solution to prevent their drying out and to minimize the oxidation of bilirubin to biliverdin. After standing over night rhythmic rings resulted as shown by the photographs reproduced in Figs. 4 and 5. In Fig. 5 the effect of the shape of the mass on the form of the bands is clearly shown. In order to secure a plane surface to photograph, in some cases a cover glass was pressed down gently on top of the specimen flattening out the high places.

A comparison of the synthetic preparations with the natural gall stones reveals a marked similarity in appearance which indicates that rhythmic banding plays a rôle in the formation of the natural stones just as it does in the synthetic ones.

The objections may be raised that there is no gelatin in natural gall stones. The answer is that the action of gelatin is not specific. It is only necessary that a protective colloid be present to inhibit the growth of the cholesterol crystals and to serve as a kind of binder. Albumin and fibrin which do occur in natural gall stones may be substituted for gelatin in the synthesis of banded stones. The specimens shown in Fig. 6 were prepared in the same way as those in Figs. 4 and 5 using instead of gelatin, 50 cc. of water in which was peptized 0.1 to 0.2 gram of fibrin.

Conclusions

From a survey of the conditions which result in the formation of the so-called "layered" stones and the experimental results given in the previous section, it would appear that the formation of such concretions is favored or initiated by inflammation, which yields irreversibly precipitated protein materials, such as fibrin and albumin. Pathologic changes bring about the precipitation of the cholesterol, carrying calcium with it, the nature of the precipitate depending upon the amount of hydrophilic colloid present. Into this mass the colloidally dispersed bile pigments diffuse and are precipitated in the form of rhythmic bands. The structure and arrangement of the bands is influenced by the shape of the mass, its density due to the pressure of other stones, and by variations in the composition of the bile fluid. After the bands are formed the structure may be invaded by radial crystallization of the cholesterol, cracks may develop, further deposition of the cholesterol may occur, or the stone may undergo alteration in other ways, producing the wide variety of forms which are found in gall bladder disease.

Summary

The following is a brief summary of the results of this paper:

1. Rhythmic rings of calcium-bile pigment and of silver chromate were obtained in a mass of cholesterol crystals precipitated in the presence of a small amount of hydrophilic colloid material such as gelatin, albumin, and fibrin.

2. The concentric rings in the "common gall stones" of inflammatory origin are not the result of the deposition of alternate light and dark colored layers but are a manifestation of the Liesegang phenomenon.

3. The colloidal bile pigments diffuse into a mass of cholesterol crystals, hydrophilic colloids and lime and the calcium-bile pigment complex is deposited in concentric bands. The term "layered stone" as applied to the "common gall stone" is a misnomer.

4. Concentric bands are not formed in either natural or synthetic cholesterole stones in the absence of hydrophilic colloids.

5. The structure and arrangement of the bands in both synthetic and natural gall stones is influenced by the density and shape of the mass, the nature and amount of hydrophilic colloid present and the composition of the bile fluid.

6. A survey has been given of the role of colloidal behavior in the formation of the so-called "pure cholesterol" and "pure pigment" stones resulting without inflammation and of the mixed colloid-crystalline stones of inflammatory origin.

The Rice Institute,
Houston, Texas.

THE MICROTOME METHOD OF THE DETERMINATION OF THE ABSOLUTE AMOUNT OF ADSORPTION

BY JAMES W. McBAIN AND C. W. HUMPHREYS

This work has been concerned with the creation of a microtome method for the determination of the absolute amount of adsorption at *static* air-water interfaces, for which no previous method existed, and with the development of this method to the point where it gives sufficiently accurate and reliable results to serve as a crucial test of the Gibbs adsorption theorem.

The validity of the Gibbs equation has never been demonstrated experimentally. In fact, as pointed out by McBain and DuBois,[1] practically all previous experimental work, where there was not an inherent error in the method used, has given observed values of the adsorption which are considerably in excess of those calculated by means of that thermodynamic equation, either in its strict form or in the approximate form commonly used. The work of McBain, Davies[2] and DuBois, corroborated by the single measurement of Harkins and Gans,[3] shows quite definitely that moving surfaces carry several times more solute than is compatible with the Gibbs equation. However, these moving surfaces, which were used in all previous measurements, may not have represented perfect equilibrium nor have met all of the conditions of the Gibbs equation. Because of the wide use of that equation, its fundamental nature, and the lack of experimental proof of it, measurements of the absolute amount of adsorption at *static* air-water interfaces are plainly needed.

The method which has been developed in this work may be outlined briefly as follows. The solution being studied is kept at rest for any desired length of time in a shallow trough of pure silver surrounded by a saturated atmosphere. By paraffining the ends of the trough the solution is made to bulge up above them without overflowing. A uniform layer 0.05 to 0.1 mm. thick is cut off from a known area (310 sq. cm.) of the surface by a small microtome blade traveling at a speed of about 35 ft. per second. This thin layer of solution is collected in a small silver-lined cylinder on which the microtome blade is mounted. The solution so obtained is weighed and its concentration is compared with that of the bulk of the solution in the trough by means of a Zeiss interferometer. From the observed difference in concentration, the absolute amount of adsorption at the surface of the solution can be calculated.

The Trough, Tracks and Microtome

The main features of the apparatus designed for this work are shown in detail in the accompanying drawings and photographs.

[1] J. W. McBain and R. DuBois: J. Am. Chem. Soc., 51, 3534 (1929).
[2] J. W. McBain and G. P. Davies: J. Am. Chem. Soc., 49, 2230 (1927).
[3] W. D. Harkins and D. M. Gans: Colloid Symposium Monograph, 6, 26 (1929).
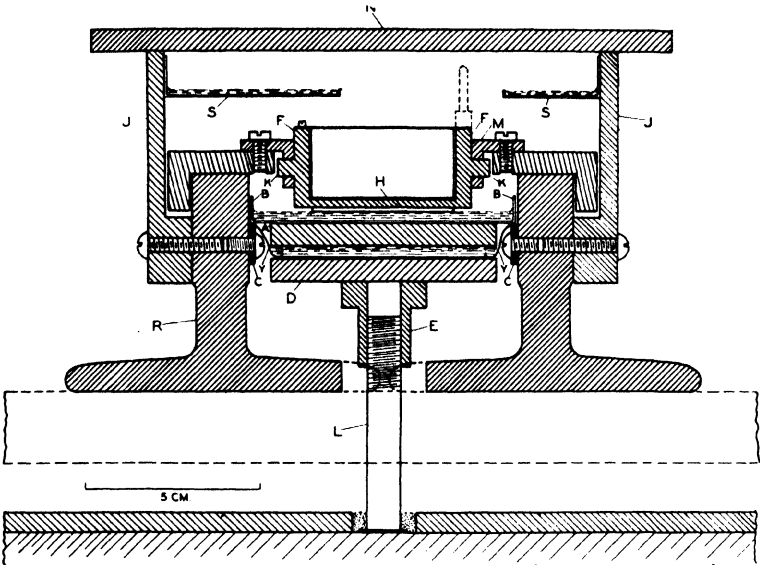
FIG I CROSS SECTION THROUGH CENTER OF INNER ENCLOSURE (THROUGH A-A' FIG 3a)
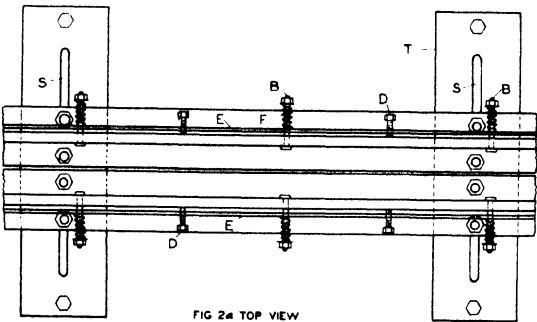
FIG 2a TOP VIEW
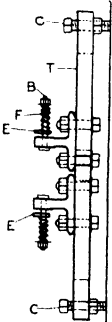
FIG 2C END ELEVATION
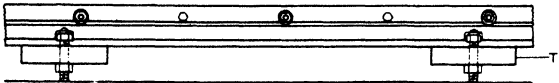
FIG 2b SIDE ELEVATION

20 CM
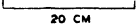
THREE VIEWS OF A SECTION OF THE TRACKS SHOWING TRACKS AND BRAKE IN DETAIL

FIG. 2

The trough B, Fig. 1, which contains the solution being used is made of pure silver 0.5 millimeters thick. It is approximately 7.5 centimeters wide, 85 centimeters long and the ends and sides are respectively three and eight millimeters high. It is supported between two heavy steel rails, R, as shown in Fig. 1. These rails are thirty-two feet long and it is upon them that the microtome carriage, which supports the microtome blade, slides. The tracks are fastened securely to steel ties at intervals of two feet as shown in Fig. 2. Near the outer edge of each tie is a set screw, C, which rests upon the concrete floor and allows adjusting of the height and leveling of the tracks. The machined upper surface of the rails was sufficiently true for the major part of the tracks. For the part adjoining the trough a much finer adjustment was necessary and was obtained by lapping this portion true so that the variation in level over the whole length of the trough was less than 0.015 mm. The upper part of both sides of the tracks are also machined.

The microtome carriage which slides along the tracks and carries the microtome blade which does the cutting is shown in detail in Fig. 6. It consists essentially of a frame, B, upon which is mounted the cylinder, C, which holds the blade. The cylinder consists of a section of one inch brass tubing, H, which is soldered at the ends to two brass disks. These disks are made with bearings, K, which fit closely through the angle pieces, M, thus allowing the cylinder to turn. The angle pieces are fastened to the carriage so that the cylinder is held firmly in place. A cover, J, made of one-half millimeter sheet silver is fastened over the remaining open part of the cylinder and curves around inside of it, thus acting as a baffle plate to keep the collected liquid from flowing out again. The microtome blade, N, is similar to a rigid safety razor blade. It fits into a small slot milled in the cylinder, as shown in Fig. 6d, and is soldered rigidly in place. The cylinder is lined with pure sheet silver and has a thin coating of paraffin so that the solution collected can be poured out more readily. The solution is removed by pouring it through one side of the same opening through which it enters. The cylinder is held in the proper position for cutting by the small steel pin, E, Fig. 6a, which rests upon the stop, S, and is held down by a thin strip of spring steel, F.

The microtome blade is given the speed necessary for cutting such a thin layer from the surface of the solution by shooting the carriage along the tracks by means of a slingshot arrangement made of rubber tubing. Since it is traveling quite rapidly (at the rate of 25 miles per hour) the carriage must be stopped rather rapidly after passing the trough. To retain the collected liquid the cylinder is turned through about 120° so that the blade and opening are pointing directly upward as soon as the trough is passed. It is turned by the steel pin, P, striking the stationary device, V, Figs. 3a and 3c, and is held in this second position by a small braking device, D and E, Fig. 6c, which has a groove in which the steel pin, P, fits.

The microtome carriage is stopped quickly but without any sudden shock by the brake shown in detail in Fig. 2. This consists of two steel strips, ten feet long, fastened to the outer sides of the rails. The braking action is exerted upon the two sides of the microtome carriage, O, Fig. 6c, which slide in the

groove between the steel strips and the rails. The desired braking action is obtained by adjusting the pressure on the sides by turning the nuts on the ends of the bolts, B, which press upon the springs, F, and by regulating the width of the groove with the set screws D.

The device, E, Fig. 3a, for stirring the solution in the trough consists of a long strip of silver, one-half millimeter thick and about two millimeters wide, just above the level of the sides of the trough, to which are fastened four cross pieces of the same material which rest upon the bottom of the trough. This long strip extends out beyond the back door and the solution is stirred by merely sliding it back and forth. The stirrer does not break the surface.

FIG 3 THREE VIEWS OF CENTRAL PORTION OF APPARATUS SHOWING GENERAL FEATURES
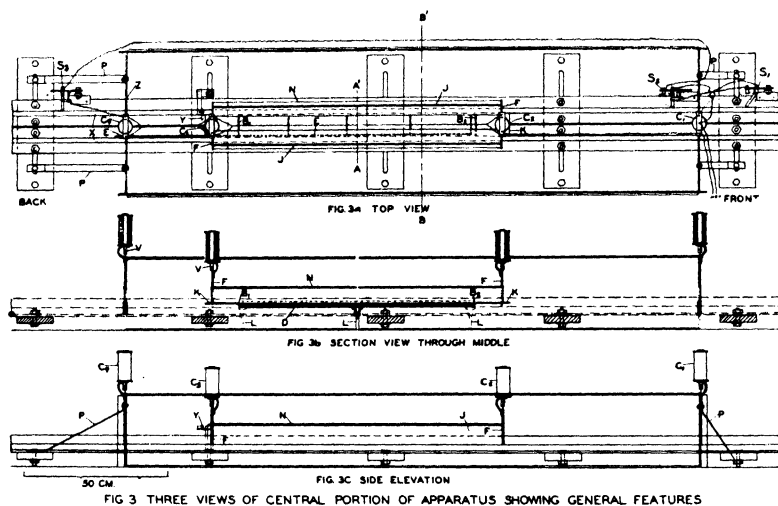
The Saturated Vapor surrounding the Trough

Since any evaporation from the solution in the trough must take place through the surface, its effect would be enormously magnified in the thin layer cut off in an experiment. Therefore it is necessary to prevent any such evaporation from taking place. The apparatus for doing this is shown in cross section in Figs. 1 and 5 and in general layout in Fig. 3. The silver trough is in an inner enclosure which is just large enough in cross section to allow the microtome carriage to pass through and extends about ten centimeters beyond each end of the trough. Around this is a much larger, plate glass, outer enclosure as shown in Figs. 3, 4 and 5, and Photographs 7 and 8. Both enclosures are nearly air-tight. The inner one is sealed off underneath the trough by the sheet of 0.001 inch thick silver foil, V, Fig. 1, which is clamped against the rails by the monel metal strips C and extends down across and upon the plate glass D, underneath the glass strips which separate the glass supports A and D. At the ends, the silver foil comes up and extends out over the ends of the silver-plated brass plates, K, Figs. 3a and 3b, upon which the doors at the ends rest. The sides of the inner enclosure are silver plated brass pieces, J, bolted to the tracks and milled out so that the microtome

carriage can pass through as shown in Fig. 1. The cover, N, is of plate glass. Vaseline is placed between the side pieces and the cover to give an air-tight fit. The sides, top and bottom of the outer enclosure are of plate glass and the ends are of silver plated brass. All exposed brass parts in either enclosure are
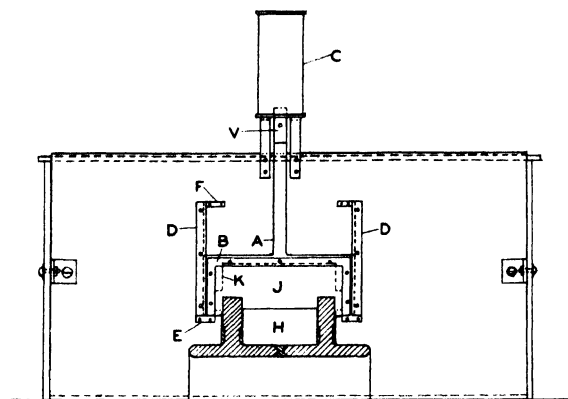
END VIEW OF OUTER ENCLOSURE SHOWING DETAILS OF DOOR

FIG. 4

20 CM.
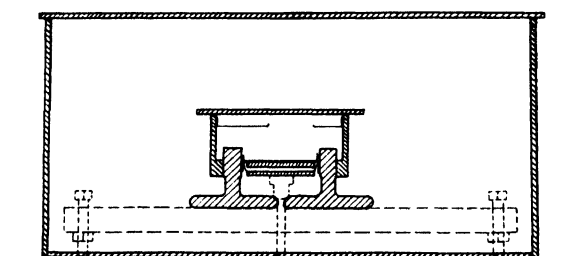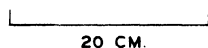
CROSS SECTION THROUGH TRACKS AND BOTH ENCLOSURES
(THROUGH B-B' FIG. 3α)

FIG. 5

silver plated to limit corrosion; such surfaces come into contact only with vapor. The solution being studied comes into contact only with pure silver or, for brief periods, with glass.

To help saturate the air space in the inner enclosure are two side trays, S, Fig. 1, filled with the solution being used. In addition, the space above the silver foil between the glass supports A and D is filled with the same solution as shown in Fig. 1. A stream of air or nitrogen saturated with respect to the

FIG 6a TOP VIEW

FIG 6c END ELEVATION

A —————————— A'

FIG 6b SIDE ELEVATION

FIG 6d CROSS SECTION THROUGH A-A' FIG 6a

5 CM   FIG 6 DETAILS OF THE MICROTOME CARRIAGE
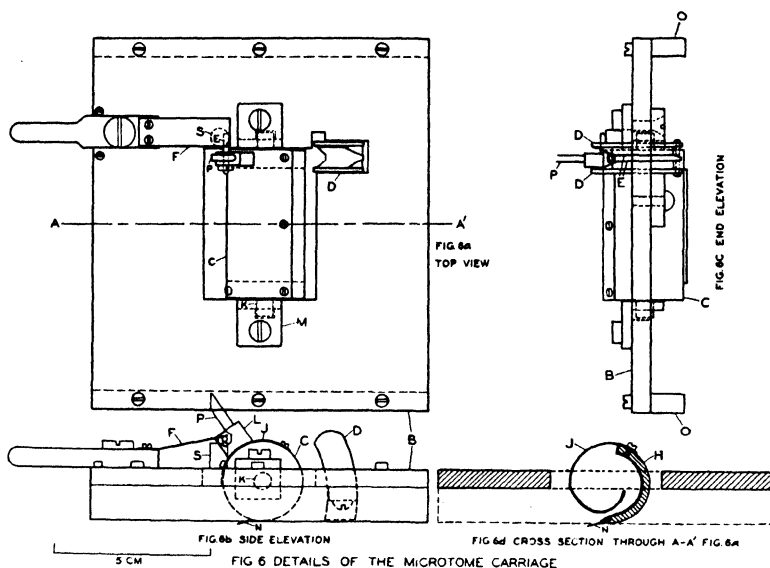
solution being used, by means of a rocking Washburn[1] saturator, may be passed into the inner enclosure also. In the large outer enclosure are a large number of crystallizing dishes, as shown in Figs. 7 and 8, which contain solution to saturate this outer enclosed air space. There are holes in the covers of both enclosures so that the whole apparatus can be set up and the solution then be put in. These holes are closed with cover glasses.

The Automatic Doors

Since the microtome carriage must pass through both enclosures in making a run, there is a close-fitting door in each end of each enclosure. These doors are automatically opened and closed by electrical contacts which are operated by the carriage itself when it is shot along the tracks. The front door to the outer enclosure is opened first and it is then closed as the other three open so there can be no rush of outside air through the apparatus to cause evaporation. A drawing of one of the doors is shown in Fig. 4 and the photograph in Fig. 8 shows quite well how they are made. A hole is cut through each of the brass
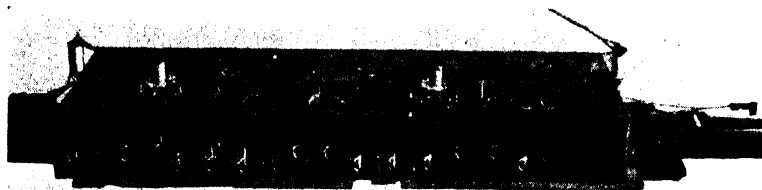
FIG. 7

[1] E. W. Washburn and E. D. Heuse: J. Am. Chem. Soc., 37, 309 (1915).

end pieces large enough to let the car through as indicated by the dotted line K in Fig. 4. The frame for the door is very light, being made of a piece of 1/32 inch duralumin A fastened to a piece of 1/16 inch duralumin B by small set screws. The frame is large enough so that the microtome carriage can pass through without touching it. It fits as closely as possible against the end piece and still moves freely. Clamped between these two parts of the frame is a piece of silver foil 0.002 inch thick which is cut out so that it fits closely around the tracks and down upon the brass block H, thus closing the opening
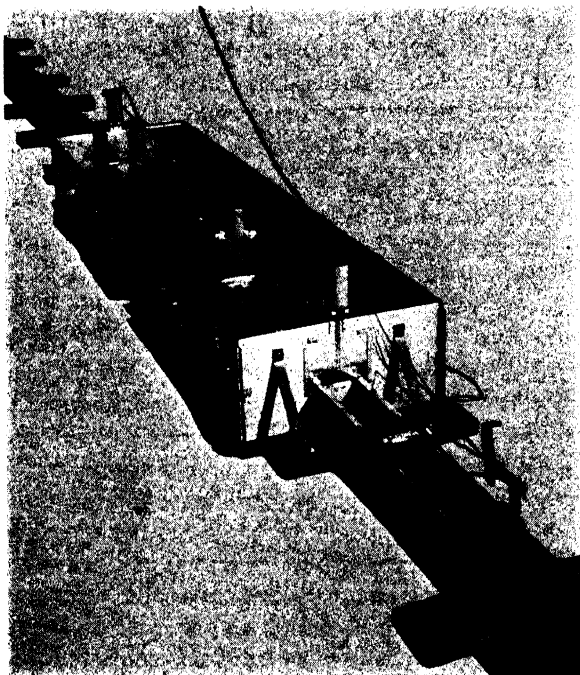
FIG 8

in the end piece. With the doors to the inner enclosure, the silver foil fits down upon the brass plates, K, Fig. 3, covered with the 0.001 inch silver foil. The doors are made of foil so that, in case they fail to open, the microtome carriage will go right through and thus not wreck any other part of the apparatus or the carriage itself. The door slides up and down in grooves milled out under the brass strips D, Fig. 4. F and E are stops.

To the top of the door frame is fastened a short piece of steel tubing, V, Figs. 4 and 3b. A coil C is fastened above this so that when a current is passed through the coil, the door is raised quickly. Each coil consists of about 2400 turns of No. 24 cotton covered copper wire and the four of them are connected in parallel to the 110 volt A.C. line. The microtome carriage operates the switches, S_1, S_2 and S_3, Fig. 3, when it is shot along the tracks and thus opens and closes the doors automatically.

Mode of Experiment

A single solution may remain in the trough for weeks or months and be subjected to varied experiments.

A single experiment is conducted as follows. About five to fifteen minutes after the last previous experiment, the amount of solution that was cut off in that run, or removed for analysis, is replaced and the solution in the trough is stirred thoroughly. It is then allowed to stand, for the gaseous phase to come into equilibrium with the solution, for a known period of time which, in the actual experiments, has varied from about twenty minutes to several days. The thin surface layer is either cut off at the end of this time or else the solution is again stirred thoroughly and allowed to stand for a known short length of time and the sample then cut off. Just before shooting the microtome carriage the cylinder is rinsed twice with solution of very nearly the same concentration as that in the trough. The run is then made as soon as possible after the second rinsing in order to allow as little evaporation as possible from any drops which may remain in the cylinder. The sample cut off is then emptied into a small weighing bottle as soon as possible. The weighing bottle has in it some of the same solution as was used for rinsing the cylinder, and this is emptied out just before the sample is poured in. It is weighed to the nearest tenth of a gram and the sample then poured into the left side of the interferometer cell. The solution in the trough is again stirred and a ten cubic centimeter sample pipetted out with which to rinse and fill the right side of the interferometer cell. The observed difference in concentration, the known weight of the sample and the known surface area cut out give necessary data for calculating the absolute amount of adsorption at the air-solution interface.

With each solution, a series of blank runs was made. A blank run is the same in every detail as a regular run except that the sample, instead of being cut off from the surface of the solution in the trough, is pipetted into the cylinder and shaken around immediately after shooting it along the tracks. This solution is then compared with a sample of the original solution. If there is a change in concentration for any solution a corresponding correction is made in the regular runs.

Calculation of Results

In a single experiment, the following quantities are measured: the weight of solution cut off (W_c); the difference in concentration (I), in grams of solute per gram of water, between the solution cut off and the bulk of the solution in the trough; and the total surface (S) cut out. Knowing the concentration of the solution in the trough (R_o), in grams of solute per gram of water, the adsorption (Γ) can be calculated by the equation:

$$\Gamma = \frac{W_c\,I}{1 + R_o + I} \cdot \frac{1}{S}.$$

At concentrations less than ten grams per thousand grams of water this may be reduced to $\Gamma = W_c\,I/S$ with a resulting error of less than one per cent.

Conditions for a Rigorous Measurement

The ideal conditions for conducting experiments using this method would be those under which the concentration of the solution in the trough would remain constant for an indefinite period of time. It might then be assumed that any difference in concentration between the sample cut off from the surface and the bulk of the solution in the trough was due to adsorption at the air-solution interface, provided there were no additional factors being introduced after cutting off the sample, as shown by blank runs. Such conditions were substantially obtained with one of the solutions studied when the concentration of the solution in the trough remained constant within about two parts per million over a period of twenty-five days during which many observations were made upon it.

It is probably correct to assume that if the concentration of the solution in the trough were increasing with time, any experiment carried out during that period would give a higher value of the adsorption than if the conditions were ideal. Conversely, if the concentration of the solution in the trough were decreasing, any experiment performed during that time would give too low a value of the adsorption. Therefore, if two series of experiments were carried out with one solution so that in one of them the conditions were such that the concentration of the solution in the trough increased very slowly and in the other it decreased very slowly, the value of the adsorption under ideal conditions would probably be between the two values so obtained.

It has been found possible to make the concentration of the solution in the trough either increase or decrease slowly with any of the solutions used by properly regulating the concentration of the solution in the trays, S, Fig. 1, with respect to that of the solution in the trough, and of that in the Washburn saturators when saturated nitrogen is passed into the enclosure. This second method therefore can be used when it is impossible to maintain ideal conditions with a solution of any substance. It was necessary to use this method in some of the experiments which have been carried out and the two values of the adsorption, obtained with the concentration of the solution in the trough increasing and then decreasing slowly, did not differ greatly.

Experimental Results

Before the addition of the large glass outer enclosure, it was impossible to maintain conditions such that the concentration of the solution in the trough would remain constant over a very long period of time. Therefore it was necessary to use the alternative procedure described above, that of controlling the conditions so that the concentration of the solution in the trough first increased and later decreased very slowly, giving two mean values of the adsorption, one of which was probably higher and the other lower than the one which would have been obtained under ideal conditions.

Since the addition of the outer enclosure, only two series of experiments have been conducted, one with hydrocinnamic acid at a concentration of 1.5 grams per 1000 grams of water and the other with the same substance at a

TABLE I

Hydrocinnamic Acid   1.5 g./1000 g. H_2O

Exp. No.	t_1	t_2	Wt. of sample	Interface change	Corrected change	Adsorption Γ g./cm$^2 \times 10^8$
1	—	22 hrs.	2.7	1.6	1.3	5.2
2	—	3½ hrs.	2.0	2.0	1.6	4.7
3	1 hr.	2 min.	2.2	1.7	1.4	4.6
4	50 min.	2 min.	2.6	1.9	1.6	6.2
5	—	4½ hrs.	2.2	2.1	1.7	5.5
6	50 min.	10 min.	1.7	2.9	2.4	6.0
7	—	11½ hrs.	2.4	1.9	1.5	5.3
8	—	2 hrs.	2.1	1.8	1.5	4.7
9	—	4¾ hrs.	2.4	1.8	1.4	5.0
10	—	12½ hrs.	2.1	2.7	2.3	7.2
11	—	7½ hrs.	2.5	2.0	1.6	5.9
12	—	4¾ hrs.	2.1	1.9	1.5	4.7
13	—	19¼ hrs.	2.4	2.9	2.5	8.9
14	—	18 hrs.	2.4	1.9	1.5	5.3
15	—	24 hrs.	2.4	1.1	0.7	2.5
16	—	47 hrs.	2.2	1.9	1.5	4.9
17	—	4¼ hrs.	2.4	2.0	1.6	5.7
18	—	7 hrs.	2.8	2.0	1.7	7.0
19	—	11¼ hrs.	2.2	2.4	2.0	6.5
20	—	12 hrs.	2.3	2.0	1.6	5.5
21	—	13½ hrs.	2.1	3.0	2.6	8.1
22	—	33½ hrs.	2.2	2.1	1.7	5.5
23	—	21 hrs.	2.4	1.9	1.5	5.3
24	—	65½ hrs.	2.4	2.0	1.7	6.0
25	—	22 hrs.	2.6	2.0	1.7	6.3
2 cm. cell						Ave. = 5.7
26	—	24½ hrs.	2.6	7.2	6.5	12.1
27	—	5 hrs.	2.3	2.3	1.5	2.5
28	—	5 hrs.	2.5	2.8	2.1	3.8
29	—	14 hrs.	2.5	2.7	2.0	3.6
30	—	25 hrs.	2.7	3.6	2.9	5.6
31	—	25 hrs.	3.1	3.0	2.4	5.3
32	—	33¼ hrs.	3.1	2.8	2.2	4.9
33	—	81 hrs.	2.8	3.1	2.5	5.0
4 cm. glass cell						Ave. = 5.4

Total Ave. = 5.6

concentration of 4.5 grams per 1000 grams of water. In the latter series of experiments, the concentration of the solution in the trough decreased steadily throughout, but only slowly. At the lower concentration, however, the conditions may be considered ideal, since the concentration of the solution in

the trough remained constant within about two parts per million over a period of four weeks. The results of this most satisfactory series of experiments to date are given in detail in Table I.

t_1 refers to the time between when the solution in the trough was last stirred after the preceding experiment and the time it was stirred shortly before that run which is under consideration. t_2 refers to the time elapsing between this second stirring and the time the sample was collected. In most of the experiments in the above table, the solution was not stirred a few minutes before the run was made. In those cases, the time between the last stirring after the preceding run and the time the run being considered was made is listed under t_2. With each solution, t_2 has had values from one or two minutes to at least several hours. None of them have shown any variation in adsorption depending upon this time interval in which the measured adsorption was allowed to take place.

The "interferometer change" is the difference between the zero reading and the reading obtained by comparing the sample collected with the bulk of the solution in the trough. The "corrected change" is obtained from the "interferometer change" by applying the correction for a blank run. With hydrocinnamic acid at the above concentration, the correction was to subtract 0.3 divisions from the observed interferometer change with the two centimeter cell and 0.6 divisions with the four centimeter cell, and in the case of a 3.0 gram sample, and proportionally more or less for a smaller or larger sample.

The last column gives the adsorption Γ at the air-solution interface as calculated from the observed weight of sample and increase in concentration of the sample over the trough solution, the surface cut out being taken as 310 square centimeters.

With the two centimeter interferometer cell which was used, a change in reading of one division with hydrocinnamic acid solution is equivalent to a change in concentration of 4.59×10^{-6} grams per gram of water. With the four centimeter cell a change of one division is equivalent to a change of 2.22×10^{-6} grams per gram of water.

The results of the above series of experiments are given in such detail to show the nature of the data obtained. They show that, under good conditions, quite consistent results can be obtained with this method.

Since no data on surface tensions of aqueous solutions of hydrocinnamic acid were recorded in the literature, such measurements were carried out by C. Bacon working in this laboratory. He used the drop-weight method as developed by Harkins and his collaborators. From these data, the values of the adsorption predicted by the approximate Gibbs equation at different concentrations were calculated.

Before the large outer enclosure was added, a great number of experiments were carried out with solutions of p-toluidine, phenol and caproic acid. The average values of the observed adsorption for the different substances at each concentration used are listed in the following table for those series of experiments in which the concentration of the solution in the trough was

changing only very slowly and was under control. In the second column is given the number of individual experiments of which the listed observed adsorption is the average value. For comparison, the corresponding values predicted by the Gibbs equation and the values obtained by McBain, Davies and DuBois, using the "bubble method," are also given. What was happening to the concentration of the solution in the trough is also shown.

TABLE II

Substance	No. of Expts.	Conc. g./1000 g. H_2O	Ave. Obs. Γ g./cm²×10⁸	Predicted Gibbs Γ	McBain and Davies	McBain and DuBois	Conc. of Sol'n in trough
p-Toluidine	11	2.00	6.1	5.2	12.6	11.8	Increasing slowly
p-Toluidine	29	1.76	4.6	4.9			Ave. for both increasing and decreasing slowly
Phenol	18	20.48	4.1	4.8		14.8	Increasing slowly
Caproic Acid	30	2.59	6.8	6.3		16.2	Constant
Caproic Acid	14	3.00	5.1	6.5		16.9	Decreasing slowly
Caproic Acid	43	5.25	6.2	6.3		20.5	Decreasing slowly
Hydrocinnamic Acid	33	1.5	5.6	5.1			Constant for four weeks
Hydrocinnamic Acid	19	4.5	5.4	7.9			Decreasing slowly

As previously stated, the above results are those in which the conditions of the experiments approached most nearly ideal conditions, or in which the concentration changes of the solution in the trough have been reversed so that the results which would have been obtained under ideal conditions could be quite closely approximated.

These results represent the only existing measurements of the absolute amount of adsorption at *static* air-water interfaces. It can be seen that, under the best conditions, the observed values have agreed quite closely with those predicted by the Gibbs equation rather than with the high values observed by McBain, Davies and DuBois and others, all of whom have been able to study moving surfaces only. They do not represent as large a body of data as that obtained by various workers with moving surfaces. However, under the best conditions, the static surfaces used here certainly approach more nearly the conditions of the Gibbs equation than do dynamic surfaces. The Gibbs equation would thus appear as a limiting law.

This method opens up a wide field for investigation. The preliminary results here reported show the desirability of further measurements of the absolute amount of adsorption at *static* air-solution interfaces, particularly over a greater range of concentration and with a great variety of solutions of all types.

Department of Chemistry,
Stanford University,
California.
May, 1931.

AN ELECTRICAL CONDUCTIVITY METHOD FOR DETERMINING THE EFFECTIVE CAPILLARY DIMENSIONS OF WOOD

BY ALFRED J. STAMM[1]

Four dynamic physical methods for studying capillary structure have been developed and applied at the Forest Products Laboratory to the determination of the effective dimensions of the fine, continuous, capillary structure of softwoods.[2,3] An electroendosmotic flow method was used for determining the effective continuous capillary cross-section of wood. Data obtained from these measurements were combined with data from hydrostatic flow studies for calculation of the average diameters of the effective openings. Although the electroendosmotic method proved to be of considerable use in determining the average and the limiting values of the various fiber lengths, it is too indirect and inaccurate a method for quantitative capillary cross-section determinations. With wood sections of low permeability, in which the resistance to flow was high, measurements of the velocity of electroendosmosis could not be made with greater accuracy than 20 per cent.[4] The determination of the increase in electroendosmotic velocity with an increase in capillary cross-section introduced another possible error resulting from the assumption that the increase in capillary cross-section caused by the drilling of fine holes in the sections could be calculated from the cross-section of the bit. The calculated increase in cross-section may have differed from the actual increase by as much as 50 per cent because of the distortion of the holes and the unavoidable tearing and brooming of the fibers. Another approximation, that of estimating the length of the effective capillaries, was necessary in combining the electroendosmosis data with data obtained from hydrostatic flow studies in order to obtain values for the average effective capillary diameters. This estimate could be made with an accuracy of approximately 50 per cent. The final calculated diameters were therefore determinable with no greater certainty than a possible error of 100 per cent. This low order of accuracy seems entirely reasonable, however, when it is realized that these openings are in general below microscopic visibility in size. Nevertheless more accurate results were desired for use in connection with a theoretical study of the rate of drying of wood. Because of this need the method described in this paper was developed.

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[2] Stamm: Colloid Symposium Monograph, **6**, 83 (1928).

[3] Stamm: J. Agr. Research, **38**, 23 (1929).

[4] O. T. Quimby, working in this Laboratory, found that the inconstancies were due to thermal and polarization effects. The use of non-polarizing electrodes might have given more accurate results, but because of the development of the new method this was never tried.

Structure of Softwoods

Electrical conductivity measurements have been used in the past for determining the ratio of the effective capillary length to the effective capillary cross-section of porous materials.[5] None of the materials investigated, however, were made up of capillaries of two such distinctly different orders of magnitude as those in wood. Because of this complication a brief consideration of the structure of softwoods is necessary.

The fiber cavities that make up the major part of the void volume of softwoods are closed at both ends, the only communication from fiber cavity to fiber cavity being through the pores in the membranes of the bordered pits. It is the size and the number of these finer openings that control the permeability of wood. Each softwood fiber with an average length of about 0.3 cm. and a diameter of approximately one hundredth of this value has from 30 to 300 pits connecting it with adjoining fibers, and there are from 50,000 to 100,000 such fibers in a square centimeter of cross-section.[6]

Fig. 1 gives a diagrammatic representation of the capillary path through wood, indicating the manner in which the fiber cavities (shown in black) are connected through the pores of the pit membranes.

Method for determining the Ratio of the Effective Capillary Length to the Effective Continuous Capillary Cross-Section

The ratio of the effective capillary length to the effective continuous capillary cross-section can be calculated from the electrical resistance of sections of wood, the voids of which are completely filled with a salt-solution, and from the specific resistance of the salt solution in bulk, providing the surface conductivity is made negligible and the conductance of the cell wall is negligible. The surface conductivity for very dilute salt solutions and especially for distilled water may be many times the bulk conductivity of the solution or of the water,[2,3,5,7,8] but for salt solutions of appreciable concentration this surface conductivity becomes negligible in comparison with the bulk conductivity. When the potassium chloride solutions used in this investigation exceeded a concentration of 0.07 mol per liter, the ratio of the specific resistance of the salt solution in bulk to its resistance in the wood structure was found to be independent of concentration, thus indicating that the surface effects are negligible. Hence measurements were made using salt solutions exceeding this concentration.

The specific conductance of dry wood is extremely small, approximately 10^{-12} mho for a cube of wood 1 cm. on an edge. When water is adsorbed by the cell wall the conductivity increases so as to give a linear relationship

[5] Fairbrother and Mastin: J. Chem. Soc., 125, 2319 (1924); Hitchcock: J. Gen. Physiol., 9, 755 (1926); Marshall: J. Soc. Chem. Ind., 46, 373T (1929).

[6] For a further description of the capillary structure of wood, see Stamm: Colloid Symposium Monograph, 4, 246 (1926).

[7] D. R. Briggs: J. Phys. Chem., 32, 641 (1928).

[8] McBain, Peaker and King: J. Am. Chem. Soc., 51, 3294 (1929); McBain and Peaker: J. Phys. Chem., 34, 1033 (1930).

between the logarithm of the conductivity and the moisture content, up to fiber saturation, at which point the specific conductance is 3×10^{-6} to 1×10^{-5} mho.[9] The water adsorbed in the cell wall at this point shows an increased conductivity over the bulk conductivity of water, because of surface conduction. Salt solutions, however, act differently. The conductivity of such solutions at the fiber-saturation point, although exceeding that of water, is sufficiently less than the bulk conductivity to make the conductivity of the cell wall in the presence of the salt negligible for the present measurements.

This fact may be illustrated by measurements made upon a transverse section of Douglas fir sapwood. The section when completely filled with a potassium chloride solution (0.199 mol per liter and 39.1 ohms specific resistance) had a resistance of 26.0 ohms. The section contained 1.907 gm. of salt solution and 1.869 gm. of water. When the section was dried to approximately the fiber-saturation point, 29.3 per cent water, the resistance was 5,100 ohms. Although the capillary cross section effective for electrical conduction was reduced in proportion to the liquid lost, the concentration of the salt was increased in the same proportion. The electrical resistance should have remained approximately constant if the liquid in the cell wall were fully as conductive as the free liquid in the cell cavities. The increase in resistance, however, is nearly two hundred fold, showing that the salt solution can not be dispersed in the cell wall in a continuous manner. Neglecting the resistance of the cell wall in parallel with the fiber-cavity resistance introduces an error of not more than 0.5 per cent.

Further evidence that solutes do not become dispersed in the cell wall in a continuous manner as water does, but on the contrary are confined to the grosser capillary spaces, is given in a previous investigation on the effect of solutes upon the apparent density of the wood substance.[10]

The electrical conductivity of a transverse wood section, the capillary structure of which is filled with a salt solution, is thus substantially equal to the sum of the bulk conductivities of the solution in all of the individual capillary paths connected in parallel. These capillary paths in turn are made up of fiber cavities and pores of pit membranes connected in series (Fig. 1). The part of the electrical resistance for which the fiber cavities are responsible can be calculated from the fractional void volume, V, which in turn can be calculated from the bulk

FIG. 1

Simplified diagrammatic representation of the capillary path through wood showing the manner in which the fiber cavities are connected through the pores of the pit membranes.

[9] Stamm: Ind. Eng. Chem. Anal. Ed., 1, 94 (1929).
[10] Stamm: J. Phys. Chem., 33, 409 (1929).

density, d, of the wood on a wet volume and dry weight basis, and the density of wood substance, d_o, which is equal to 1.52 gm.per cu. cm. Thus,

$$V = 1 - d/d_o \qquad (1)$$

The fractional void volume obtained in this way includes all void structure. For softwoods free from resin ducts this void volume is made up mostly of fiber cavities, together with the water-filled void structure of the swollen cell wall and the void volume of the ray cells. The ray cell voids, which amount to only 1 or 2 per cent of the total, have been neglected to simplify the calculations.

The fractional void volume of the cell wall is equal to the product of the moisture content, M, per gram of dry wood at the fiber-saturation point, and the density of the wood, d. Then the fractional void volume of the fiber cavities per cubic centimeter of wood

$$V_f = V - Md \qquad (2)$$

This void volume is made up of a longitudinal component of 1 centimeter, and radial and tangential components that approach equality. The void cross-section of the average fiber cavity for transverse sections

$$q_f = V - Md \qquad (3)$$

Then the electrical resistance of the combined fiber cavities

$$R_f = \frac{R_{sp}L}{(V - Md)Q} \qquad (4)$$

where R_{sp} is the specific resistance of the salt solution, L the number of unit thicknesses of the section under investigation, and Q the number of unit cross-sections of the specimen.

The total resistance, R_m, of the salt solution in the pores of the pit membranes will depend upon the fractional cross-section of such pores traversed in parallel and the length of path, that is, the continuous effective capillary cross-section, q_m, of the pores expressed as a fraction of the cross-section of the specimen, and the sum, l_m, of the thicknesses of the pit membranes traversed in series. Then,

$$R_m = \frac{R_{sp}l_m}{Q \; q_m} \qquad (5)$$

The experimentally measured resistance, R, is equal to the sum of the resistances from equations (4) and (5).

$$R = \frac{R_{sp}L}{(V - Md) \; Q} + \frac{R_{sp}l_m}{Q \; q_m} \qquad (6)$$

and

$$\frac{l_m}{q_m} = \frac{Q}{R_{sp}} \left(R - \frac{R_{sp}L}{(V - Md) \; Q} \right) \qquad (7)$$

for transverse sections.

For radial sections, where the flow of current is in the tangential **direction,** equation (7) takes a somewhat simpler form since

$$R_f = \frac{R_{sp}L \ \sqrt{V - Md}}{Q \ \sqrt{V - Md}} = \frac{R_{sp}L}{Q} \tag{8}$$

and therefore

$$\frac{l_m}{q_m} = \frac{Q}{R_{sp}} \left(R - \frac{R_{sp}L}{Q} \right) \tag{9}$$

Although the radial and the tangential components of the void volume are not exactly equal, they may be considered so for this calculation, since R_f is so small in comparison with R_m that a deviation of 50 per cent in R_f will cause an error in R_m of only 2 per cent.
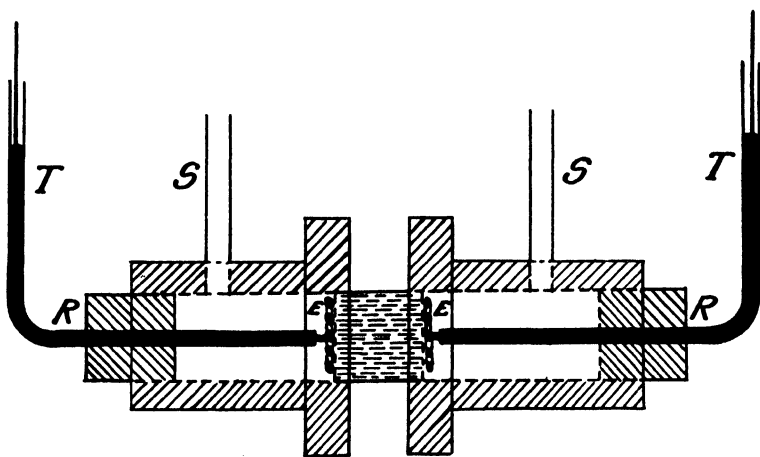
FIG. 2
Cells used in electrical resistance measurements.

The measurements were made upon wood sections that were clamped between the faces of two hard rubber cells and upon cylindrical sections that had been turned in a lathe in a soaked and swollen condition to fit tightly into the ends of the cells (Fig. 2). Several sets of cells and electrodes of different cross-section were used for the measurements. The electrodes, E, were made of heavy platinum wire wound in the form of disk coils and sealed into glass tubes, T, that were filled with mercury for electrical contact. The electrodes were fitted into the cells with rubber stoppers, R. The side tubes, S, served in filling the cells with the salt solutions. The electrodes were freshly platinized each day before using. The measuring apparatus consisted of a student circular slide-wire bridge, a four-dial resistance box (0.1 to 999.9 ohms), a microphone hummer, telephone receivers, a condenser, a switch, and dry cells connected according to standard conductivity measuring practice.

The sections were soaked in distilled water for at least two weeks. To facilitate the replacement of air by water the soaking was done in a vacuum desiccator to which suction was applied intermittently. Potassium chloride

was then added. Electrical resistance measurements on the wood sections showed that diffusion was complete and equilibrium of the salt distribution was obtained in less than a week. The specific resistance of the salt solution in equilibrium with the wood sections was determined, using the hard-rubber cells of Fig. 2 clamped together with a ring gasket replacing the wood section. Measurements were made with the electrodes separated by different distances. All measurements were made at 25° C in a thermostatic air bath.

Experimental Results

The differences between measurements made with broad transverse sections clamped between the faces of the cells and cylindrical sections cut to fit the cells were first investigated. Current in the broad sections fanned out appreciably beyond the area bounded by the cells. The extent of the spreading of the current proved to be a function of the specific electrical conductivity and of the thickness of the sections and was independent of the cross section of the cell. It is thus possible to correct for this spreading of the current for transverse sections when measurements are made on the same specimen with cells of two different cross sections. Although the extent of the spreading will increase from zero at each of the surfaces of the section to a maximum at the center, it is simpler for these calculations to consider an average effective extent of spreading X. This must be added to each of the cell radii in order to calculate the effective cross section. Then,

$$\left(\frac{r_1 + X}{r_2 + X}\right)^2 = \frac{R_2}{R_1} \tag{10}$$

where r_1 and r_2 are the cell radii of two different cells and R_1 and R_2 are the corresponding resistances. Table I gives the specific resistances calculated in this manner, using three different sizes of cells, as well as the results obtained from measurements made on transverse cylindrical sections cut to fit the cells. The values obtained by the two methods agree quite well. There is a slight tendency, however, for the specific resistance to be slightly less for the cut sections; this will be considered again later in this article.

Measurements made in equilibrium with two different concentrations of salt solution are given in Table II. The results agree within experimental error for the concentrations used.

The values of l_m/q_m for different thicknesses of the transverse sections are plotted in Fig. 3 for all of the Sitka spruce data given in Table I and Table II, together with data for two other Sitka spruce specimens of different density and two species of cedar. The data in all cases show a linear relationship between l_m/q_m and the thickness of the section; the graphs when extrapolated to zero thickness pass through the origin. This indicates that the continuous effective capillary cross section, q_m, varies but slightly for adjoining sections and that the length of the effective capillaries, l_m, varies directly with the thickness of the section, thus indicating a rather uniform distribution of

TABLE I

Comparison of the Specific Electrical Resistance of Transverse Sections of previously Seasoned and Resoaked Sitka Spruce calculated from Measurements made upon Cylindrical Sections cut to fit the Cells and Sections extending beyond the Cell Cross-Sections.

Density of the wood (volume green and weight oven-dry)—0.297 gm. per cu. cm.
Concentration of potassium chloride solution—0.81 mol per liter
Specific resistance of potassium chloride solution—10.31 ohms

Kind of section	Thickness of section	Radius of cell	Measured resistance	Extent of spreading X	Effective area of cross section	Calculated specific resistance of section	l_m/q_m
	Cm.	Cm.	Ohms.	Cm.	Cm.²	Ohms.	
Extending	0.615	0.870	4.01	0.0398	2.600	16.96	
		.430	15.00	{ .0398 / .0399 }	.694	16.92	} 0.151
		.245	40.80	.0399	.255	16.92	
	1.062	.870	6.00	.1030	2.974	16.80	
		.430	20.00	{ .1030 / .1037 }	.896	16.87	} .248
		.245	46.80	.1037	.382	16.82	
	1.481	.870	7.75	.137	3.186	16.70	
		.430	24.50	.137	1.010	16.70	} .333
Cut	1.481	.870	10.40	.000	2.378	16.68	.323
Extending	2.031	.870	10.48	.156	3.307	17.07	
		.430	32.10	.156	1.079	17.05	} .523
Cut	2.031	.870	14.40	.000	2.378	16.85	.484
		.430	58.80	.000	.581	16.82	.480

equally unobstructed capillaries. Such a relationship is rather to be expected, considering the large number of fiber cavities and pit membranes traversed by the current.

The ratio l_m/q_m per unit thickness for the specimens of Sitka spruce of different density varies directly with the density (Fig. 3 and Table III). The simplest explanation of this relationship is that the pit membrane thicknesses vary directly with the density, while q_m remains practically constant. Values of q_m, however, will vary from species to species.

Fig. 4 and Table IV show the differences in the ratio l_m/q_m for sapwood and heartwood. The differences in effective capillary cross section are surprisingly small, thus indicating that the large differences in the permeability of sapwood and heartwood are due to another cause. This matter will be considered in more detail later in this article.
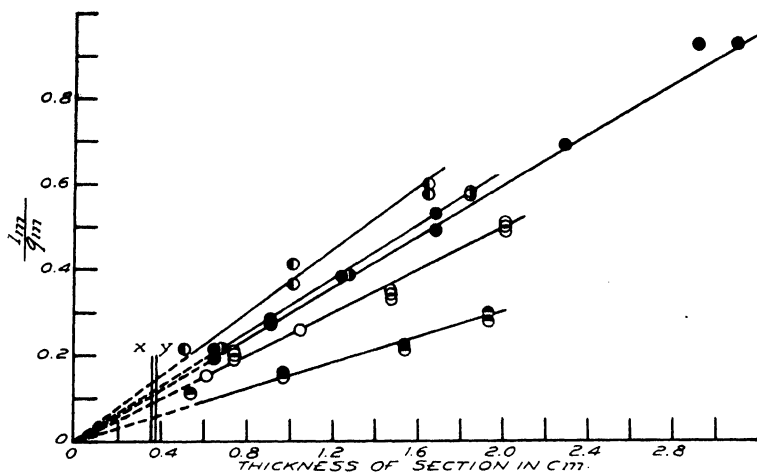
FIG. 3

Relationship between the ratio of the effective capillary length to the effective continuous capillary cross section, and the thickness of the section, for spruce and cedar.

    O Sitka spruce, density 0.297 gm. per cu. cm.
    ● Sitka spruce, density 0.347 gm. per cu. cm.
    ◑ Sitka spruce, density 0.370 gm. per cu. cm.
    ◐ Alaska cedar, density 0.442 gm. per cu. cm.
    ◒ Western red cedar, density 0.290 gm. per cu. cm.
    x Average fiber length for Alaska cedar
    y Average fiber length for Sitka spruce and western red cedar
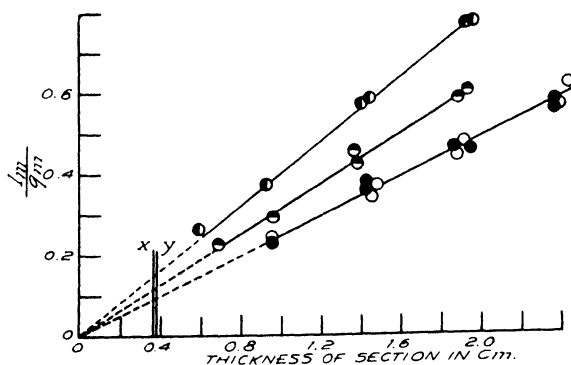
FIG. 4

Relationship between the ratio of the effective capillary length to the effective continuous capillary cross section, and the thickness of the section, for Douglas fir and slash pine.

    O Coast Douglas fir, sapwood
    ● Coast Douglas fir, heartwood
    ◒ Slash pine, sapwood
    ◐ Slash pine, heartwood
    x Average fiber length for pine
    y Average fiber length for Douglas fir

TABLE II

Measurements made in Equilibrium with Two Different Concentrations of
Salt Solution upon previously Seasoned and Resoaked Transverse
Sections of Sitka Spruce cut to fit the Cells.

Density of the wood (volume green and weight oven-dry)—0.297 gm. per cu. cm.

Thickness of section	Radius of section	Concentration of potassium chloride in mols per liter	Specific resistance of potassium chloride solution	Resistance of section	l_m/q_m
Cm.	Cm.		Ohms.	Ohms.	
0.751	0.870	0.810	10.31	5.4	0.196
	.430	.810	10.31	22.1	.194
	.870	.134	58.00	30.4	.197
	.430	.134	58.00	123.7	.187
1.481	.870	.810	10.31	10.4	.323
	.870	.134	58.00	58.8	.340
	.430	.134	58.00	240.5	.335
2.031	.870	.810	10.31	14.4	.484
	.430	.810	10.31	58.8	.480
	.870	.134	58.00	81.3	.492
	.430	.134	58.00	332.0	.491

TABLE III

Effect of the Density of previously Seasoned and Resoaked Sitka Spruce upon
the Ratio of the Effective Capillary Length to the Effective
Continuous Capillary Cross Section

Density of specimen	l_m/q_m for average fiber length	Column 2 values / Column 1 values
Gm. / Cm.³		
0.297	0.091	0.306
.347	.108	.312
.370	.115	.311

<div align="center">TABLE IV</div>

Comparison of Measurements Made upon Unseasoned Transverse and Radial Sections of the Sapwood and the Heartwood of Slash Pine

Sapwood, density (volume green and weight oven-dry)—0.456 gm. per cu. cm.

Average number of fibers and rays traversed per mm. in the tangential direction—34.0

Heartwood, density (volume green and weight oven-dry)—0.430 gm. per cu. cm.

Average number of fibers and rays transversed per mm. in the tangential direction—33.0

Concentration of potassium chloride solution—0.79 mol per liter

Specific resistance of potassium chloride solution—9.84 ohms

Part of wood	Section	Thickness of section	Radius of section	Resistance of section	l_m/q_m	l_m/q_m per pit membrane traversed in series	
						Observed	Corrected
		Cm.	Cm.				
Sap	Transverse	1.940	0.92	15.00	0.608		
		1.365	.92	10.65	.453		
		.960	.92	7.38	.292		
		.640	.92	5.05	.229	[1]0.055	
		1.890	.46	58.50	.588		
		1.395	.46	43.00	.426		
Heart		1.965	.92	15.30	.783		
		1.450	.92	11.30	.587		
		.922	.92	7.20	.375		
		.585	.92	4.68	.267	[1].070	
		1.925	.46	59.90	.771		
		1.400	.46	43.80	.575		
Sap	Radial	1.830	0.92	163.0	42.2	0.0677	
		.750	.92	68.7	17.8	.0698	[2]0.0810
		1.380	.46	416.0	26.8	.0571	
		.970	.46	306.0	19.7	.0578	
Heart		1.680	.92	158.5	41.2	.0743	
		1.240	.92	118.5	30.8	.0752	[2].0927
		1.230	.46	391.0	25.2	.0622	
		.900	.46	289.0	18.6	.0627	

[1] For a travel of half the average fiber length; taken from Fig. 3.

[2] For the average diameter of the fibers and rays traversed, corrected for leakage of surface current across the sections.

Table IV gives also the data for radial sections of both the sapwood and the heartwood of slash pine. The values for l_m/q_m in this case were obtained from equation (9). The number of fibers and ray cells traversed in the tangential direction per unit of distance was determined by direct microscopic

measurements upon transverse microtome sections.[11] The values of l_m/q_m per membrane traversed in series for the sections turned on a lathe so as to fit the cells vary with the radius of the cell, because of a slight leakage of current over the cylindrical surface of the sections. Assuming the thickness of this leakage film to be the same for both cells, the total leakage current will vary directly as the circumference and consequently as the radius of the cell. The leakage per unit of cross section, however, will vary inversely as the radius of the cell. Therefore,

$$\frac{1}{R_1} - C = \frac{1}{R_2} - \frac{r_1}{r_2} C \tag{11}$$

in which R_1 and R_2 are the measured resistances reduced to unit dimensions for the cells with radii r_1 and r_2, respectively, and C is the leakage conductance for r_1. This conductance, in general, amounts to 18 to 20 per cent of the total conductance. Presumably there is a similar surface leakage of current with the transverse sections previously considered, but because the resistance of those sections is less than a tenth of the resistance of the radial sections, the error will be less than 2 per cent. This fact will account for the tendency for the measurements on the cut sections given in Table I to be slightly less than those for the broad sections. No measurements were made on broad radial sections because the necessary correction would be complicated by the longitudinal spreading of the current, which is greater than the spreading in the radial direction on account of the difference in conductivity in these two directions.[12]

The reason for the deviations between the values for l_m/q_m per membrane traversed in series for the transverse and the radial sections is that the values for the transverse sections were calculated by assuming a uniform distribution of the pit membranes along the length of the fiber. Only with such distribution does the current pass on the average through no more than one pit membrane in traversing a distance of half a fiber length. Microscopical observations, however, have shown that the pits are much more numerous near the ends of the fibers, thus actually requiring a greater section thickness than half a fiber length for the current to pass on the average through even one pit membrane. The flow conditions can perhaps be better understood by considering the current that passes through the fiber cavities as being made up of a bundle of threads in parallel, each thread entering a fiber cavity through a single pit membrane opening and leaving through an opening in another pit membrane. A thread may enter at one pit and leave through the nearest pit or it may enter through a pit close to one end of the fiber and leave through a pit at the other end. Hence the possible paths for these filament currents vary from a negligibly short length to practically the full fiber length; the actual location of the pits, of course, gives an average length of path greater than the uniform location assumed.

[11] These measurements are further described in "A New Method for determining the Proportion of the Length of a Tracheid that is in Contact with Rays," by Stamm, Botanical Gazette, **92**, 101 (1931).

[12] Stamm: Ind. Eng. Chem., **19**, 1021 (1927).

An approximation of the actual value of q_m can be made from the value of l_m/q_m for transverse sections taken from the graphs for a section whose thickness is equal to that of half the average fiber length, and from the thickness of a single pit membrane, which was found microscopically to range from 2×10^{-5} to 2×10^{-4}cm.; it would perhaps be better to use l_m/q_m for radial sections having a thickness of the average fiber and ray diameter. Dividing l_m by l_m/q_m gives a value of q_m ranging from 0.3×10^{-3} to 8.0×10^{-3} for all of the species studied. The electroendosmosis method gave values of q_m ranging from 0.9×10^{-3} to 1.7×10^{-3}.[2,3] This agreement is quite satisfactory when the large uncertainty of the effective value of l_m is considered.

Effective Capillary Dimensions

The preceding data for l_m/q_m were combined with data from hydrostatic flow studies[2,3,13] to calculate the average effective capillary radii. Measurements were also made by the method for overcoming the effect of the surface tension of water in the capillary system to obtain the maximum effective capillary radii. All of the data are assembled in Table V. The maximum radii range from about 1 to 6 times the average radii. The radii obtained by overcoming the effect of surface tension decrease with an increase in the thickness of the section. This is to be expected; the most effective path through a number of pit membranes in series will approach the average effective path as the number of pit membranes in series increases, because of the decreasing probability of all the pit membranes in series containing pores of maximum size. For example, measurements made upon radial sections, in which the tangential displacement of water by gas is through the same structure, except that far more pit membranes are traversed in series per unit thickness of the section, gave a value of r for the heartwood of slash pine of 4.0×10^{-6} and for the sapwood of 3.7×10^{-4}. The number of pit membranes traversed in series for these sections was approximately 40. The data thus show that the radii obtained by the method of overcoming the effect of surface tension approach the values obtained by the electrical conductivity and the hydrostatic flow method. The fact that these two entirely different methods of measuring the size of the effective openings give results of the same order of magnitude provides confirmation of the validity of the methods.

The data further show the large differences in the effective capillary dimensions for the sapwood and the heartwood of slash pine. The difference between the capillary dimensions of the sapwood and the heartwood of the Douglas fir specimens is much less. This can be partially attributed to the presence of ring shakes, that is, cracks between the annual rings in the heartwood, which tends to increase the heartwood values. Treatment of Douglas fir with creosote indicates that for this species there is an appreciable penetration through ring shakes.

[13] Stamm: Physics, 1, 116 (1931).

ALFRED J. STAMM

Table V

Effective capillary sizes from hydrostatic flow and from overcoming of surface tension

Species of wood	Density of section	Thickness of section L	Effective cross section Q	Standard capillary constant r_2^4/l_2	Extrapolated pressure drop ratio P_2/P_1	l_m/q_m (from Fig. 2 and Fig. 3)	Average effective capillary radius	Pressure to overcome surface tension	Maximum effective capillary radius
	$Gm./Cm^3$	$Cm.$	$Cm.^2$				$Cm.$	$Kg./Cm.^2$	$Cm.$
Slash pine heartwood unseasoned	0.430	1.340	2.08	0.53×10^{-9}	0.013	0.540	2.37×10^{-6}	27.0	5.5×10^{-6}
	.430	.875	2.08	.53	.025	.350	2.65	22.0	6.7
	.430	.670	2.08	.53	.037	.270	2.83	15.5	9.5
	.430	.670	2.08	3.73	.0047	.270	2.66	—	—
								Cm. of mercury	
Slash pine sapwood unseasoned	.456	1.980	2.08	32.1	1.25	.620	2.19×10^{-1}	12.0	9.0×10^{-1}
	.456	1.365	2.08	32.1	1.70	.430	2.11	11.2	9.7
	.456	.915	2.08	32.1	2.40	.290	2.04	10.2	10.6
	.456	.730	2.08	32.1	2.85	.230	1.97	9.5	11.4
								Kg./Cm.²	
Coast Douglas fir heartwood unseasoned	.326	2.490	1.54	3.73	.010	.610	6.83×10^{-6}	20.5	7.18×10^{-6}
	.326	1.820	1.54	3.73	.012	.450	6.43	19.5	7.55
	.326	1.480	1.54	3.73	.017	.360	6.83	19.0	7.75
	.326	1.000	1.54	3.73	.023	.245	6.56	18.0	8.18
	.326	.740	1.54	3.73	.033	.180	6.73	17.0	8.65
Coast Douglas fir sapwood unseasoned	.403	1.830	1.54	3.73	.10	.450	1.86×10^{-5}	9.0	1.84×10^{-5}
	.403	1.460	1.54	3.73	.13	.360	1.89	8.0	1.84
	.403	.950	1.54	3.73	.20	.235	1.90	7.0	2.10
	.403	.707	1.54	3.73	.27	.175	1.90	3.5	4.20
Alaska cedar seasoned and resoaked	.442	1.218	2.08	1.93	.0017	.435	1.47×10^{-6}	40.0	3.7×10^{-6}
	.442	.873	2.08	1.93	.0035	.310	1.78	43.0	3.4
	.442	.582	2.08	1.93	.0090	.210	2.35	37.0	4.0
Western red cedar heartwood seasoned and resoaked	.290	1.090	2.08	.81	.010	.160	1.40×10^{-6}	—	—
	.290	1.067	2.08	1.99	.0022	.160	1.03	28.0	5.2×10^{-6}
	.290	.795	2.08	1.99	.0045	.115	1.25	21.0	7.0
	.290	.610	2.08	.81	.024	.090	1.63	—	—
Sitka spruce heartwood seasoned and resoaked	.347	1.885	2.08	3.73	.0025	.555	2.80×10^{-6}	17.0	8.6×10^{-6}
	.347	1.130	2.08	3.73	.0035	.330	2.56	13.0	11.3
	.347	1.130	2.08	.53	.025	.330	2.58	—	—

Summary

1. A method has been developed for determining the ratio of the effective capillary length to the effective continuous capillary cross section by means of electrical resistance measurements of salt solutions filling the wood structure, and the resistance of the solutions in bulk.

2. Measurements made upon sections cut to fit the electrode cells and sections extending beyond the effective area of the cells agree when a correction is made for the spreading of the current in the oversize sections.

3. The concentration of the salt solution does not affect the results when it exceeds 0.07 mol per liter.

4. The ratio l_m/q_m for a single species varies directly with the density of the wood.

5. The values of the ratio l_m/q_m do not differ greatly between the sapwood and the heartwood.

6. The values of the ratio l_m/q_m per pit membrane traversed, calculated from measurements made upon tangential and radial sections, agree quite well.

7. Combining the data for l_m/q_m with data obtained from hydrostatic flow studies gives the average radii of the effective capillaries. These values are compared with the maximum effective radii obtained by the method of overcoming the effect of surface tension. The maximum values range from about 1 to 6 times the average values and approach more nearly the average values when the measurements are made under conditions in which a large number of pit membranes are traversed in series. The effective radii of pit membrane pores are larger for sapwood than for heartwood, the difference varying with the species.

Madison, Wis.

THE PARTICLE SIZE AND CONSTITUTION OF
COLLOIDAL FERRIC OXIDE. I[1]

BY J. B. NICHOLS, ELMER O. KRAEMER, AND E. D. BAILEY

It is generally recognized that an adequate interpretation of the properties and behavior of a colloidal solution is impossible without accurate information concerning the particle sizes of the dispersed material. Furthermore, the processes by which a colloidal solution may be formed can not be completely understood unless the changes in particle size during the successive stages of formation can be quantitatively followed.

Up to the present time, methods for measuring particle size have generally been limited in applicability, uncertain in accuracy, and often quite useless for quantitatively determining the non-uniformity in particle size. This has been particularly true for the colloidal solutions in which particle size approaches atomic dimensions and the behavior peculiar to the colloidal state is most pronounced. The invention and development of the ultracentrifuge during recent years by Svedberg and his associates[2] has provided a group of methods for determining particle size which promises to avoid many of the weaknesses of the earlier methods and to constitute the most powerful and most generally applicable technic for investigating dispersity in colloidal solutions. In Svedberg's laboratory attention has been focussed primarily on colloidal solutions of organic macromolecular materials, especially the proteins. With the exception of Rinde's work on colloidal gold,[3] no detailed ultracentrifugal investigations of inorganic colloids have yet been published.

There can be no doubt that ultracentrifugal methods will be as effective for the inorganic colloids as for the organic ones. The most attractive group of inorganic colloids for ultracentrifugal investigation is perhaps that of the so-called hydrous oxides, which include the oxides and hydroxides of beryllium, aluminum, silicon, vanadium, chromium, manganese, iron, cobalt, nickel, and most of the higher elements in the same groups of the periodic table. The hydrous oxides have been the subject of practically continuous study since the pioneering work of Graham. During the last few years they have been even more extensively investigated.[4] On account of the dearth of reliable data concerning particle size and the wealth of data available on other aspects, ultracentrifugal analysis of the hydrous oxides should be particularly useful.

For initiating research in this field, we have selected colloidal ferric oxide. It has been studied as thoroughly as any other hydrous oxide; its formation by boiling a sufficiently dilute solution is relatively simple; its color offers advantages in connection with the ultracentrifugal analysis. The chemical composition of the dispersed phase in these colloidal solutions is to a consider-

[1] Communication No. 65 from the Experimental Station of the E. I. duPont de Nemours and Company.

[2] Svedberg: "Colloid Chemistry," 2nd ed. (1928); Kolloid-Z., 51, 10 (1930).

[3] Rinde: "The Distribution of the Sizes of Particles in Gold Sols," Diss., Upsala (1928).

[4] Symposium on oxyhydrates, Z. angew. Chem., 42, 595, 885 (1929); Weiser: "The Hydrous Oxides" (1926).

able extent uncertain. In part, at least, it is sometimes a basic salt, sometimes a hydroxide, sometimes anhydrous ferric oxide. In this paper we shall use the term colloidal ferric oxide or hydrous ferric oxide, without desiring to imply, however, that the particles are in all cases simply Fe_2O_3 carrying adsorbed materials.

The introductory investigation, reported in this paper, dealt with colloidal solutions formed on hydrolysis of boiling dilute ferric chloride solutions. The particle-size determinations involved analysis of both the sedimentation velocity and the sedimentation equilibrium in the ultracentrifuge. The effect on particle size of duration of boiling, concentration of ferric chloride solution, and reversal of charge was determined. To obtain better insight into the hydrolytic changes, chemical analysis of the intermicellar liquid was carried out. In continuation of the investigation, attention will be given to other methods for forming the colloidal ferric oxide, the effects of dialysis and of aging, flocculation and peptization, solvation, and other such topics susceptible to ultracentrifugal analysis.[1]

Experimental

The low-speed type of ultracentrifuge used throughout this investigation is similar to that described by Svedberg and Heyroth[2] and yields a maximum centrifugal force about 10,000 times that of gravity. For the determination of the particle-size distribution curves of the ferric oxide the following modified form of Stokes' law was used:[3]

$$r = \sqrt{\frac{9\,\eta\,\ln\left(\dfrac{x+a}{a}\right)}{2\,(d_p - d_m)\,\omega^2 t}}$$

where r is the radius of the particle in cm., η the viscosity of the medium, d_p the density of the particle, d_m the density of the medium, ω the angular velocity $(= 2\,\pi n/60$, where n is the centrifuge speed in r.p.m.$)$, t the time of centrifuging in seconds, x the distance in cm. along the cell from the meniscus, and a the distance of the meniscus from the axis of rotation.

The micellar or particle weight is determined from the sedimentation equilibrium by the relation[4]

$$M = \frac{2RT\,\ln\dfrac{c_2}{c_1}}{(1 - V\rho)\,\omega^2\,(x_2^2 - x_1^2)}$$

For spherical particles, $M = 4/3\pi \cdot r^3\,d_p\,N$, where M is the micellar weight, N is the Avogadro number, R the gas constant $(= 83.19 \times 10^6)$, T the absolute temperature, V the partial specific volume of the substance, ρ the density of the solution, c_2 and c_1 the concentrations at the points x_2 and x_1 distant from the axis of rotation of the centrifuge.

[1] Cf. Nichols: Colloid Symposium Monograph, 6, 287 (1928).

[2] J. Am. Chem. Soc., 51, 550 (1929).

[3] For the theory underlying the determination of distribution curves by means of the ultracentrifuge, see Svedberg and Rinde: J. Am. Chem. Soc., 46, 2681-85 (1924); Rinde: "The Distribution of the Sizes of Particles in Gold Sols," Diss., Upsala (1928); and Svedberg: "Colloid Chemistry," 171 (1928).

[4] Svedberg and Fåhraeus: J. Am. Chem. Soc., 48, 430; Svedberg and Nichols: 3081 (1926); Svedberg: Kolloid-Z., 51, 10 (1930).

Most of the ultracentrifuge determinations were made at a speed of 10,000 r.p.m., corresponding to a force about 5,000 times gravity. The two sedimentation-equilibrium runs were made at speeds of 1950 r.p.m. and 2800 r.p.m. to give a favorable range of concentration in the final equilibrium.

A preliminary value of 4.5 was used for the density of the ferric oxide particles, which represents the estimates of Wintgen[1] and of Dumanskii[2] and our own pycnometric data. This value is uncertain owing to the difficulty of making proper allowance for hydration in the determination of the concen-
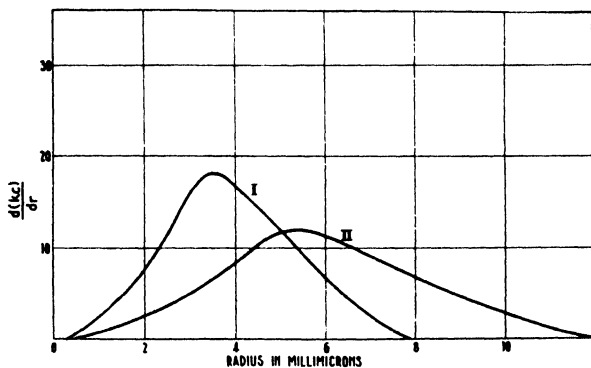
FIG. 1

Effect of the Density assumed on the Weight-Optical Distribution Curve of Ferric Oxide from 0.037 M FeCl$_3$ hydrolyzed One Hour at the Boil

Curve	Density	Mean Radius	Area
I	4.5	3.8 mμ	64%
II	2.5	5.8	64

tration of colloid in the sol. It may therefore be necessary later to alter this value somewhat as a result of density determinations now in progress by procedures which take into consideration the hydration of the particles. To give an idea of the effect the assumed density will have on the distribution curve, Fig. 1 is presented. It represents the weight-optical distribution curve of the primary particles of sol Fe-30 prepared by the hydrolysis of 0.037 M FeCl$_3$ solution. The distribution curve corresponding to the real density will undoubtedly fall somewhere between the limits shown. Until more accurate data are available, however, the distribution curves for a density of 4.5 will serve as a satisfactory means for studying relative changes in the dispersity produced by various treatments.

The particle-size distribution curves obtained from the ultracentrifuge have been designated as *weight-optical* distribution curves because in a polydisperse system of particles the light absorption may change with radius. Since, therefore, they ordinarily do not represent the true relation of weight of material to radius, the term "weight-optical" has been introduced to call attention to the fact that an apparent concentration is determined which is the product of the absorption constant k of the given radius by the concen-

[1] Kolloidchem. Beihefte, **7**, 266 (1915).
[2] Kolloid-Z., **8**, 232 (1910).

tration c of material of that radius. If the particles of the substance are fairly uniform in size, or if the light absorption is nearly constant over a range of sizes, then the weight-optical distribution curve will coincide with the weight-distribution curve.

Formation of the Colloid

Effect of Duration of Hydrolysis: A stock solution of approximately two-molar ferric chloride was prepared at the start of the work. The ferric oxide sols were made by diluting portions of this stock, adding the dilute FeCl$_3$ to boiling water, and hydrolyzing at 100° under a reflux condenser to prevent the loss of water and of hydrochloric acid formed during the hydrolysis. The hydrolytic action was stopped, after drawing off the sample, by cooling rapidly to room temperature.
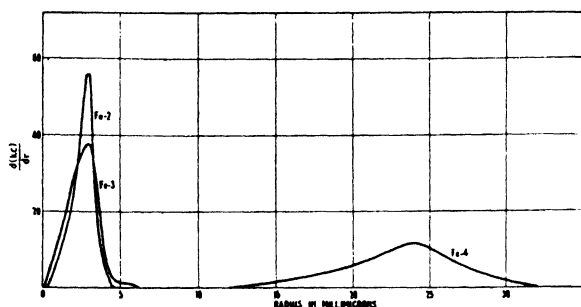
FIG. 2

Effect of Time of Hydrolysis on the Weight-Optical Distribution Curves
of Ferric Oxide from FeCl$_3$

			Mean Radius	Area
(Fe-2)	16 min.	Hydrolysis	2.7 mμ	87%
(Fe-3)	60 "	of 0.005 M	2.6	94
(Fe-4)	24 hrs.	FeCl$_3$ at the boil	23.0	96

Fig. 2 gives the distribution curves obtained for the ferric oxide sols drawn off after sixteen minutes, one hour, and 24 hours of hydrolysis of 0.005 M FeCl$_3$ solution. The difference in area from 100% is due to non-centrifugible material. All samples were centrifuged without dilution. It is evident that there was very little growth in the particles between 16 minutes and one hour of hydrolysis, but by 24 hours' digestion there was a large growth, from 2.6 to 23 millimicrons mean radius. X-ray analysis of the colloid coagulated with potassium sulfate and dried at 105° showed a change from an essentially amorphous structure for the one-hour sample to a micro-crystalline hematite. The increase in particle size is therefore principally due to growth of the primary particles. Part of the increase, however, may result from flocculation, for x-ray analysis would not reveal the presence of some flocculated material accompanying the crystalline portion, and ultracentrifugal analysis would not distinguish between flocculated material and single crystals.

When a more concentrated solution was hydrolyzed there was such a rapid growth in particle size or agglomeration that, after eight hours' digestion,

most of the ferric oxide was in the form of a coarse, brick-red sediment. This sediment was too coarse to ultracentrifuge as a water dispersion; therefore, preparatory to the determination of particle size, it was washed and redispersed in 95% glycerin of viscosity roughly 250 times that of water. Fig. 3, giving the distribution curves for sols obtained after a one-hour and an eight-hour hydrolysis of 0.037 M FeCl$_3$ solution, shows a growth in mean size from 4.4 to 132 millimicrons. When these distribution curves are plotted on a more open scale, they resemble in form the other curves presented. An x-ray examination of the coarser, brick-red material from the eight-hour hydrolysis showed it
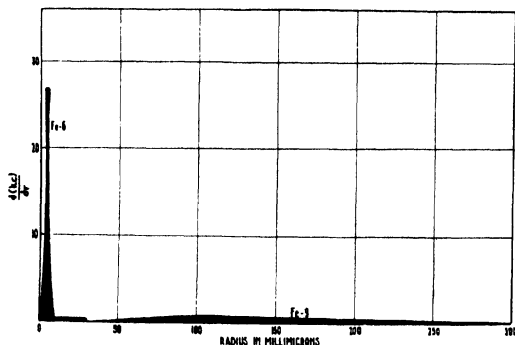
FIG. 3

Effect of Time of Hydrolysis on the Weight-Optical Distribution Curves of Ferric Oxide from 0.037 M FeCl$_3$

Sample	Time of Hydrolysis	Mean Radius	Area
(Fe-6)	1 hr.	4.4 mμ	90%
(Fe-9)	8 "	132	89
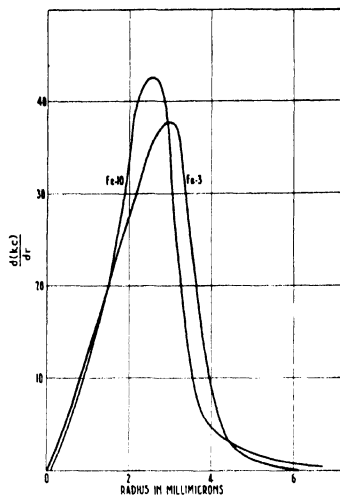
FIG. 4

Reproducibility of Ferric Oxide from 0.005 M FeCl$_3$ Hydrolyzed One Hour at the Boil

	Mean Primary Radius	Area	Uncentrifugible Material
(Fe-3)	2.6 mμ	89%	<4%
(Fe-10)	2.4	85	ca.10

to be entirely hematite. The colloid formed by the one-hour hydrolysis also gave a more distinct x-ray diagram than was obtained by hydrolysis of the more dilute FeCl$_3$ solution; its composition was that of a hydrous ferric oxide, but the pattern has not as yet been identified. It is possible that it may represent an expanded lattice[1] of hematite or goethite.

The reproducibility of the hydrolytic process is demonstrated by Figs. 4 and 5. The second hydrolysis for each concentration was made approximately two months after the first and from the same stock ferric chloride solution. The agreement is reasonably good as is evident from the curves. In the more concentrated sols there always seems to be a small amount of coarser material which sediments too rapidly to permit the obtaining of more detailed information than simply the mean size under the experimental conditions required for proper investigation of the distribution of primary particle sizes. Accordingly this coarser, probably flocculated portion is indicated as a rectangle of the proper relative area at the right of the primary distribution curve.

[1] Simon and Schmidt: Zsigmondy Festschr. Kolloid-Z., **36**, 55 (1925).

This coarser material undoubtedly would be the only portion visible under the ultramicroscope, because even highly diffracting gold particles of 4 milli-microns radius are scarcely visible under the ultramicroscope.
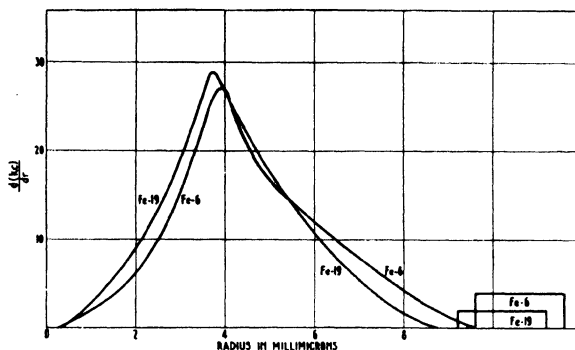
FIG. 5

Reproducibility of the Ferric Oxide from 0.037 M FeCl$_3$ hydrolyzed
One Hour at the Boil

	Prim. M. Rad.	Prim. Area	Sec. M. Rad.	Sec. Area
(Fe-6)	4.4 mμ	90%	ca.20 mμ	8%
(Fe-19)	4.05	95	—	4
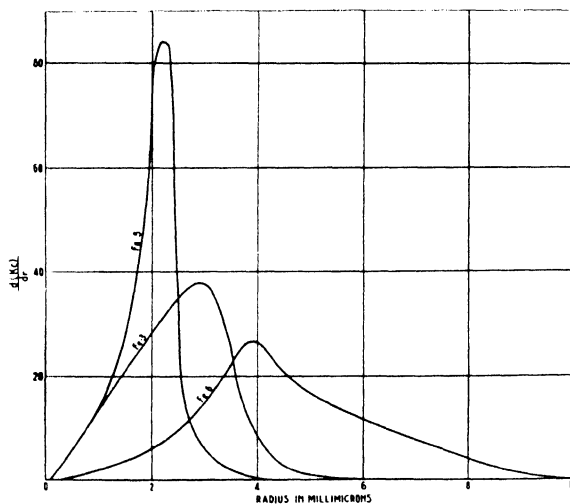
FIG. 6

Effect of Concentration during Hydrolysis on the Weight-Optical Distribution
Curves of Ferric Oxide from FeCl$_3$

		Mean Radius	Area
(Fe-5) −0.003 M	FeCl$_3$	2.0 mμ	85%
(Fe-3) −0.005 M	hydrolyzed	2.6	94
(Fe-6) −0.037 M	one hour at the boil	4.4	90

Effect of Concentration of Ferric Chloride: The distribution curves (two of which have been shown above) of ferric oxide obtained from the one-hour hydrolysis of ferric chloride solutions, covering a 13-fold concentration range

up to 0.037 M FeCl$_3$, are combined in Fig. 6 to indicate the effect of concentration. Even with the assumption throughout of the same density of 4.5, there is only a two-fold increase in radius from 2.0 to 4.4 millimicrons, corresponding to about a ten-fold increase in weight. It is likely, however, that the sols prepared from the lower concentrations of ferric chloride also have a lower density and are therefore nearer to the mean size of the more concentrated sol than is indicated in the figure; that is, the apparent difference in distribution curves may in part be due to a difference in hydration or in swelling of porous particles.

The general inferences to be drawn from the curves presented in the last two sections are: First, the hydrolytic process is rapid and probably is com-
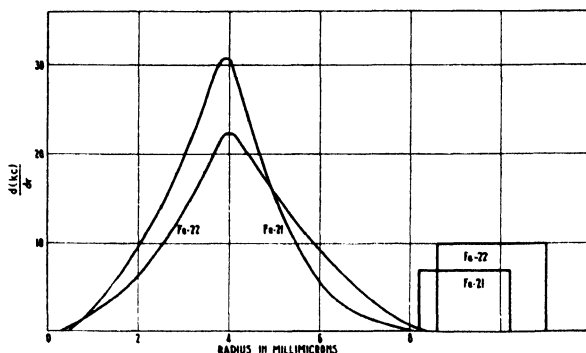
FIG. 7

Comparison of the Weight-Optical Distribution Curves of Ferric Oxide before and after Reversing the Charge with Potassium Citrate

	Charge	Prim. M. Rad.	Prim. Area	Sec. M. Rad.	Sec. Area
(Fe-21)	Positive	3.8 mμ	84%	ca.20 mμ	14%
(Fe-22)	Negative	4.2	76	ca.20	24

plete in the first hour; second, the succeeding digestion favors the secondary processes of dehydration, development of crystallinity, and growth of crystal size; third, the secondary aggregation and aging phenomena proceed more rapidly as the concentration of hydrolyzable material is raised.

Reversal of Charge: All of the sols described thus far have been the ordinary, positively charged sols stabilized with ferric or hydrogen ion. It is relatively easy, however, to reverse the charge with potassium citrate and obtain a negative sol stabilized with citrate ion. The resulting sol has much the same appearance as the original, positively charged sol, that is, a clear red color with only a faint muddy cast in reflected light. A fresh stock solution of ferric chloride was prepared and a solution of 0.04 M FeCl$_3$ was hydrolyzed at the boil. This sol was studied in the ultracentrifuge the following day and a portion of the sol was made 0.1 molar with respect to potassium citrate by adding molar potassium citrate to the original sol. The light absorption of the sol, now nine-tenths as concentrated as initially, was practically identical with that of the original sol, the increase in light absorption being due mostly to the production of greenish-yellow ferric citrate from the iron present in the intermicellar liquid.

Fig. 7 gives the distribution curves obtained for the two sols. The two curves are similar in form, the reversed sol having a slightly larger mean size of 4.2, as compared with 3.85 millimicrons for the original sol, and a greater amount of large, probably flocculated material of about 20 millimicrons radius. It seems likely that if the potassium citrate solution and the ferric oxide were mixed instantaneously and if the citrate concentration were adjusted more carefully then identical distribution curves could be obtained for a positive and a negative sol. If these two sols are mixed immediate flocculation of course occurs. On standing, there is a redistribution of ions resulting in a partial repeptization.

Donnan Effect

The sols prepared from the hydrolysis of ferric chloride were studied in their original condition without any attempt to remove salts by dialysis both because a hydrolysis-aggregation would probably occur and because a Donnan
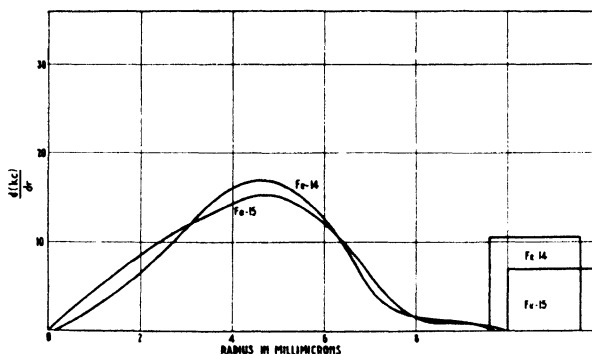
FIG. 8
Effect of Sodium Chloride on the Weight-Optical Distribution Curve of Aged Ferric Oxide from 0.037 M FeCl$_3$ hydrolyzed One Hour at the Boil

	Concn. NaCl	Prim. M. Rad.	Prim. Area	Sec. M. Rad.	Sec. Area
(Fe-14)	None	4.6 mμ	76%	ca.19 mμ	21%
(Fe-15)	0.1 M	4.2	77	ca.19	14

potential might enter into the centrifuging of a purified sol arising from the partial separation of the large colloidal ions from small inorganic ions.[1] In order to make sure that enough salts were present in the sols to repress this possible electrical potential, molar sodium chloride solution free from sulfate was added to give final solutions 0.01 M or 0.1 M with respect to sodium chloride.

Fig. 8 gives a comparison of the distribution curves of an aged ferric oxide sol (from the first hydrolysis of 0.037 M FeCl$_3$) with and without the addition of sodium chloride. It is evident that there is no appreciable change in the distribution curve, but there appears to be a slight increase in secondary material of about 20 millimicrons in radius shown in the squares at the right. A similar study was made on the dilute sol prepared from 0.005 M FeCl$_3$. If a Donnan effect were present the addition of sodium chloride would produce a shift in the distribution curve to larger particle sizes, but in the presence of

[1] Cf. Tiselius: Z. physik. Chem., **124**, 457 (1926).

0.1 molar sodium chloride there was actually a slight decrease in mean radius to about 2.4 millimicrons; therefore, it is safe to conclude that all the sols contain sufficient electrolyte to repress any Donnan effect which might arise from the separation of charges.

Effects of Dilution

It is often mentioned that dilution of colloidal material produces a disaggregation, so an attempt was made to ascertain whether a colloidal ferric oxide would change in particle size on dilution.

Fig. 9 shows the distribution curve obtained for a two-months old sol (I from 0.037 M FeCl$_3$) compared with the curves for the same sol diluted to
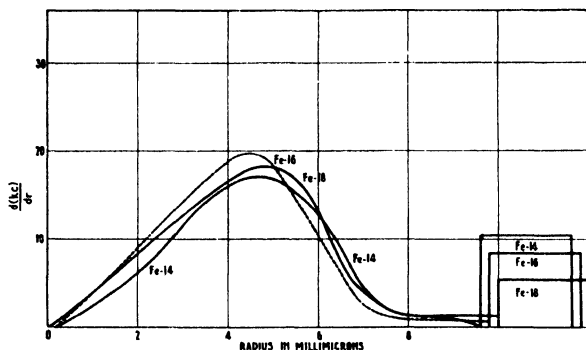
FIG. 9

Effect of Dilution on the Weight-Optical Distribution Curve of Aged Ferric Oxide from 0.037 M FeCl$_3$ hydrolyzed One Hour at the Boil

	Dilution	Prim. M. Rad.	Prim. Area	Sec. M. Rad.	Sec. Area
(Fe-14)	None	4.6 mμ	76%	ca.19 mμ	21%
(Fe-16)	¼ with water	4.2	81	16	17
(Fe-18)	¼ with 0.05N HCl	4.45	82	ca.20	11

one-quarter of the initial concentration with water (the dotted curve) or with 0.01 N hydrochloric acid, which is approximately the acidity of the intermicellar liquid. There seems to be no appreciable change when the sol is diluted with hydrochloric acid except a possible repeptization of some of the secondary material of about 20 millimicrons radius shown at the right of the curve. However, there seems to be a slight decrease in mean size from 4.6 to 4.2 millimicrons accompanying the dilution with water. It is possible that this change had not reached completion at the time of the centrifuging.

Sedimentation-Equilibrium Experiments

In order to eliminate trouble with a possible hindered diffusion of the larger particles of the sol and rather large diffusion for the smaller particles, sedimentation-equilibrium runs were made. The more dilute sols give abnormal sedimentation-velocity curves which, on inspection, seem to represent a range of very small, easily diffusible particles, and some material which exhibits hindered diffusion and sedimentation.

Figs. 10 and 11 and Tables I and II describe the final equilibria obtained for the two dilute sols prepared respectively from 0.003 M FeCl$_3$ and 0.005 M

FeCl₃. In the same figures is also plotted the variation in apparent micellar weight with distance along the length of the cell. A mean micellar weight was calculated from the concentration gradient over the region of the cell in which the original concentration obtained at equilibrium. (This procedure was found permissible by comparing the sedimentation-equilibrium curves for known mixtures). The mean radius obtained from the mean micellar weight was larger in each case, 3.1 and 3.4 millimicrons as compared with 2.0 and 2.4 millimicrons from the sedimentation-velocity method, for the original,
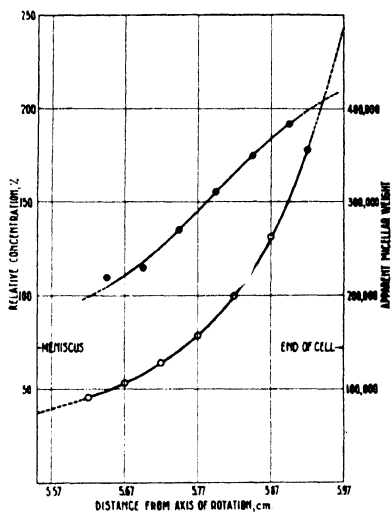
FIG. 10
Sedimentation-Equilibrium of Ferric
Oxide from 0.003 M FeCl₃ hydrolyzed
One Hour at the Boil (Fe-20)
○ Variation of relative concentration with
distance along the cell.
-●- Variation of apparent micellar weight
with distance along the cell.
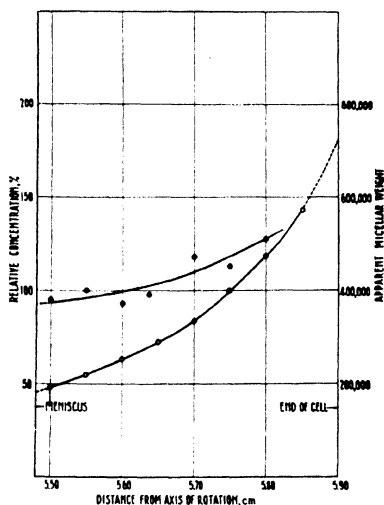
FIG. 11
Sedimentation-Equilibrium of Ferric
Oxide from 0.005 M FeCl₃ hydrolyzed
One Hour at the Boil (Fe-23)
○ Variation of relative concentration
with distance along the cell.
-●- Variation of apparent micellar weight
with distance along the cell.

freshly hydrolyzed sols (Fe-5 and Fe-10). However, a redetermination of the mean particle size of the more concentrated sol, Fe-10, by the sedimentation-velocity method shortly after the completion of the sedimentation-equilibrium runs showed that the distribution curve had shifted slightly on aging from 2.4 to 2.8 millimicrons mean radius. Thus the discrepancy is not so large between the values obtained by the two methods. The residual difference between 2.8 and 3.4 millimicrons is very likely caused by the assumption of too high a density (4.5) for the particles. An analysis of the results from the two methods is being carried out to enable us to obtain a more reliable value of the density and the radius of the more or less hydrated particles in the sols.

Composition of the Intermicellar Liquid

The composition of the intermicellar liquid in a three-months old sol (Fe-30) obtained from the second hydrolysis of 0.037 M ferric chloride was investigated from several angles: namely, ultrafiltration, flocculation with potassium sulfate, and optical analysis of the non-centrifugible portion in the ultracentrifuge.

TABLE I

Sedimentation Equibrium of Ferric Oxide (Fe-20)

0.003 M FeCl$_3$ hydrolyzed for one hour at the boil and diluted to one-half; speed 2800 r.p.m., ($\omega= 93.3\ \pi$); mean centrifugal force, 4.950 $\times 10^5$ dynes, distance of meniscus from center of rotation, 5.55 cm.; length of column, 0.42 cm.; thickness of cell, 0.8 cm.; density of Fe$_2$O$_3$ taken as 4.5, making $V=0.222$ (prelim.); $T = 303.1°$; photographic records taken 32, 40.5, 49.5 hrs. after the start; Eastman Process plates, Eclipse developer, 2 min. development.

Distance from axis of rotation, cm.		No. of exposures	Mean relative concn., %		Micellar weight
x_2	x_1		c_2	c_1	M
5.92	5.87	5	177.1	131.2	383,900
5.87	5.82	10	131.2	100.0	350,000
5.82	5.77	10	100.0	78.7	311,200
5.77	5.72	10	78.7	64.1	270,600
5.72	5.67	10	64.1	53.8	230,300
5.67	5.62	10	53.8	45.7	219,100

TABLE II

Sedimentation Equilibrium of Ferric Oxide (Fe-23)

0.005 M FeCl$_3$ hydrolyzed one hour at the boil and diluted to one-half; speed 1950 r.p.m. ($\omega = 65\ \pi$); mean centrifugal force, 2.373 $\times 10^5$ dynes; distance of meniscus from center of rotation, 5.48 cm.; length of column, 0.42 cm.; thickness of cell, 0.8 cm.; same density and V assumed as in Table I; $T = 303.1°$; photographic records taken 33.5, 39.5, 41.5, 48 hrs. after the start; plates and development same as in Table I.

Distance from axis of rotation, cm.		No. of exposures	Mean relative concn., %		Micellar weight
x_2	x_1		c_2	c_1	M
5.85	5.80	11	143.2	118.3	510,400
5.80	5.75	11	118.3	100.0	451,600
5.75	5.70	11	100.0	84.0	472,400
5.70	5.65	11	84.0	72.8	393,300
5.65	5.60	11	72.8	63.6	373,300
5.60	5.55	11	63.6	55.0	401,400
5.55	5.50	5	55.0	48.3	380,800

For the ultrafiltration a Giemsa ultrafilter[1] obtained from Carl Schleicher and Schüll Company was arranged so that a pressure of one atmosphere could be applied to the ferric oxide sol to force the liquid through the filter. Under the experimental conditions used about 15 cc. of ultrafiltrate an hour was obtained, the latter portion of which was slightly more colored than the earlier portions, probably resulting from the large increase in concentration of extremely small ferric oxide particles on the pressure side of the membrane towards the end of the filtration. In view of this increase in color the ultrafiltrate was sent through the filter again and a much lighter yellow filtrate was obtained.

[1] Biochem. Z., **132**, 488 (1922).

Another portion of the sol was flocculated with an equal quantity of 0.0025 molar potassium sulfate, the precipitate centrifuged down to a compact mass, and the supernatant liquid poured off and saved for analysis and measurement of light absorption.

The only means available for determining the composition of the non-centrifugible material in the sol was the measurement of its absorption in the long-wave ultraviolet while the sol was being centrifuged. An attempt was made to collect a few drops of the liquid above the sedimented material at the end of a run in the ultracentrifuge, but the amount was too small to obtain an analysis on it. It should be possible, however, with a thicker cell to obtain enough liquid for a microanalysis of the chlorine content and perhaps a colorimetric analysis of the iron content.

The iron analyses were made by the Knop[1] dichromate method with diphenylamine as indicator, because neither the potassium permanganate titration nor the thiocyanate colorimetric method gave reliable results. Table III gives the analytical and optical data obtained for the intermicellar liquid. The analytical results obtained on the content of iron and chlorine in the ultrafiltrate and the supernatant liquid from the coagulation are expressed in terms of gram-equivalents per liter. The optical concentrations of the ultrafiltrate, of the supernatant liquid corrected to its original concentration before dilution with the coagulating potassium sulfate solution, and of the non-centrifugible material in the liquid above the sedimenting ferric oxide in the ultracentrifuge are expressed in terms of the per cent of parent ferric oxide sol possessing equal light absorption.

TABLE III

Composition of the Intermicellar Liquid of Aged Ferric Oxide Sol II (Fe-27)

Liquid	Analytical Concentration		Relative Light Absorption Equiv. to Fe_2O_3 Concn.	
	Fe Concn. g.eq./l.	Cl Concn. g.eq./l.	366 mμ	435 mμ
Aged Fe_2O_3 Sol II	0.1161	0.1123	100%	100%
Ultrafiltrate	0.0719	0.1066	31.5	6.5
Supernatant Liquid	0.0733	0.1125	31.7	6.5
Non-centrifugible	—	—	37.0	8.0

The analyses given in Table III show that the ultrafiltrate and the supernatant liquid from the coagulation have nearly the same iron content. As might be expected, however, the supernatant liquid contains more chlorine than the ultrafiltrate, owing to the displacement of chloride from the micelle upon the addition of the coagulating sulfate ion.[2] The chlorine content of the supernatant liquid corresponds very closely to the total chlorine present in the sol, thus indicating almost complete displacement of chlorine from the micelle at coagulation. The slightly lower content of iron in the ultrafiltrate undoubtedly results from a small adsorption of semi-colloidal ferric oxide on the ultrafilter.

[1] J. Am. Chem. Soc., **46**, 263 (1924).

[2] Cf. Linder and Picton: J. Chem. Soc., **87**, 1908 (1905); Weiser: J. Phys. Chem., **35**, 10 (1931).

The absorbing material present in the ultrafiltrate and in the supernatant liquid from the coagulation was practically identical, as measured by the light absorption both in the long-wave ultraviolet and in the blue region of the spectrum; both solutions possessed absorptions equivalent to practically the same per cent of that of the original ferric oxide sol. The ultraviolet light absorption of the ultrafiltrate was equivalent to one-half the concentration of ferric chloride employed in the preparation of the ferric oxide sol. On the other hand, analytical data showed 62% of the total iron to be present in the ultrafiltrate of this aged sol. These facts indicate that the iron compound present in the ultrafiltrate is less absorbing than that present in the sample of the six-months old stock ferric chloride solution freshly diluted to the concentration used for the hydrolysis. In other words, the freshly diluted ferric chloride contains a small amount of partly hydrolyzed iron. This portion would tend to be eliminated by re-solution in the excess of hydrochloric acid present during the aging of the ferric oxide sol.

As mentioned above, the third method of investigating the composition of the intermicellar liquid depended on the measurement of the ultraviolet light absorption of the solution in the meniscus region of the centrifuge cell after the sol had been centrifuged five hours at 10,000 r.p.m., a treatment which would remove colloidal material having a micellar weight greater than a few thousand from this region. The table shows that the relative light absorption of the remaining semi-colloidal, non-centrifugible material was somewhat greater than that of the supernatant liquid from the coagulation or of the ultrafiltrate. In the blue region of the spectrum the absorbing material of the meniscus solution is equivalent to 8% of that contained in the whole sol, as compared with 6.5% for the other two liquids, and in the ultraviolet it is equivalent to 37% of the whole sol, as compared with 31.5% for the other two liquids. The ratios are practically the same for the two wave lengths, but the magnitude is different because of different relative absorptions of ferric chloride and colloidal ferric oxide for the two wave lengths. The lower light absorption possessed by the ultrafiltrate may result from the adsorption of some semi-colloidal ferric oxide by the filter during ultrafiltration. Similarly, the equally low light absorption shown by the supernatant liquid may result from the removal by occlusion of some of this same material during coagulation with potassium sulfate. It would seem that the simple removal of colloidal material by centrifuging represents the mildest treatment of the system.

A general consideration of the ultracentrifugal, analytical, and light-absorption data indicates that ferric oxide sols formed by boiling dilute ferric chloride solutions contain unchanged ferric chloride, hydrochloric acid formed by the hydrolysis of the ferric chloride, and three principal colloid-fractions: a very highly dispersed fraction, which is non-centrifugible under the conditions of this investigation and which is perhaps a ferric hydroxyl chloride: the major fraction, having a particle size within the range of 1 to 10 millimicrons; and a coarser portion, which is probably formed by aggregation of the principal fraction. The light absorption of the principal fraction is very much greater than that of an equivalent amount of ferric chloride; the light ab-

sorption of the semi-colloidal material is intermediate in magnitude. The proportions of these constituents depend on the concentration of the initial ferric chloride, the duration of digestion, and the age of the sol. Prolonged heating is conducive to dehydration of the ferric hydroxide portion of the colloid-fractions, aggregation of the primary particles, and development of crystallinity. The hydrolytic process involves typical mass action effects; pH is a controlling factor in determining the amount of nascent $Fe(OH)_3$ or $Fe(OH)_xCl_{(3-x)}$ which precipitates out to form the colloidal matter. During the aging which occurs at room temperature unpublished data indicate that re-solution of the colloidal ferric oxide to ferric chloride proceeds to an appreciable extent. The semi-colloidal fraction is probably most sensitive to this process. Greater initial concentration of ferric chloride, with the consequent production of more hydrochloric acid, causes this re-solution to proceed more rapidly and to a greater extent.

It is a pleasure to acknowledge the assistance given by two of our associates. The chemical analyses were made by Mr. E. S. Wilkins of our analytical department. The x-ray analyses were carried out by Dr. A. W. Kenney.

Summary

1. An ultracentrifugal study has been made of the particle-size distribution of undialyzed ferric oxide prepared by the hydrolysis of ferric chloride under different conditions.

2. It was found that the sols were reasonably reproducible, that dilution had no appreciable effect on the distribution curves, and that sufficient electrolyte was present in the undialyzed sols to eliminate any Donnan effect during centrifuging.

3. The hydrolytic process is rapid; subsequent digestion favors the secondary processes of dehydration and growth of crystal size.

4. X-ray analysis showed that the first particles formed in the hydrolysis were some form of hydrous ferric oxide which, on prolonged digestion, was converted into crystalline hematite.

5. The size of the primary particles (a few millimicrons in radius) produced in the first stages of the hydrolysis is not greatly influenced by the concentration of ferric chloride, but the rate of growth of the particles is much increased by higher concentrations of hydrolyzable material.

6. A sol reversed in charge by means of potassium citrate was found to have nearly the same distribution curve as the original, positively charged sol.

7. Sedimentation-equilibrium runs made on two sols gave approximately the same mean size as the sedimentation-velocity method.

8. Analytical and light-absorption data obtained on the intermicellar liquid indicate that the sol contains a semi-colloidal fraction approaching the dispersity of $FeCl_3$ in addition to the primary and secondary portions determined in the ultracentrifuge. The relative proportions depend on concentration, duration of digestion, and aging.

Wilmington,
Delaware.

THE CONCENTRATION OF CATIONS IN CLAY SOLS*

BY RICHARD BRADFIELD

The application of certain inorganic salts to infertile soils often causes an increase in the growth of the crops. The failure of plants to make optimum growth on such soils is believed to be due to the fact that some essential ion is present in insufficient concentration to permit of its sufficiently rapid absorption for optimum growth. The response to fertilizer salts is commonly attributed to the fact that they increase the concentration of some essential ion at the disposal of the plant.

At first sight it would seem a simple matter for the chemist to examine an infertile soil in the laboratory and to make definite recommendations regarding its fertilizer requirements on the basis of these laboratory tests. Such attempts are usually far from satisfactory however. We have not yet been able to find a solvent for extracting the soil which resembles sufficiently closely the extracting power of the plant. We will consider here but one of the thousands of such attempts that have been made in the last century.

It has been found that the soil solution, i.e., the solution bathing the soil particles at water contents favorable for plant growth, can be displaced in apparently unaltered form by the use of the proper displacing technique. This displaced solution however frequently contains less of certain essential ions than is found necessary for good growth by solution culture studies in which the concentration of the cultural solution is maintained by continuous renewal. Such observations have raised the question as to the concentration of these essential ions on the surface of the soil particle. The relation between the plant root and the soil is a very intimate one. The plant root is known to give off considerable amounts of CO_2 which in contact with water would form H_2CO_3 which, in turn, could furnish both anion and cation for replacing other essential ions from the surface of the soil particle. The efficiency of such a mechanism would be undoubtedly influenced by the concentration of ions at the surface of the soil particles.

It has been clearly demonstrated[1] in the case of carefully purified hydrogen-clays that the concentration of hydrogen ions in a clay paste may be 1000 times as great as that in the ultrafiltrate from such a paste. It would seem probable from these results that the concentration of other cations might also be greater at the surface of the clay particles than in the intermicellar liquid. The results reported in this paper represent a preliminary effort to determine the order of magnitude of the concentrations encountered. It is planned to make a more exhaustive study of the problem.

[1] Bradfield: J. Phys. Chem., **35**, 364 (1931).

That the colloidal clay particles make an appreciable contribution to the conductivity of clay sols is shown by a comparison of the specific conductivity of a sodium-clay and its ultrafiltrate:

$$K \times 10^{-4}$$

Na—Marion clay sol .022 N. 3% by wt.   2.37

Ultrafiltrate from above sol   1.00

That there is considerable conductance at the surface of colloidal clay particles has frequently been observed during the electrodialysis of clays. In a direct current field the clay particles are deposited on the anode membrane, apparently in a definitely oriented form. Finger-like projections are formed which if undisturbed will tend to bridge across the space between the membranes almost completely. These projections are frequently branched. Bubbles of gas can often be seen at their ends. If the current density has been high these deposits are usually rather dense and appear very much dehydrated when compared with a fresh deposit. If these bridging projections are broken by means of a stirring rod they fall to the bottom and until they have had an opportunity to become reoriented there is a very noticeable lowering in the amount of current thru the cell.

The following experiment illustrates the same phenomena. Two perforated platinum electrodes about 1 cm square and held rigidly about 2 cm. apart were dipped into a dilute H-Bentonite sol and 110 volts D.C. applied at the electrodes. In a few minutes practically all of the clay had collected on the anode and the space between the electrodes was almost completely bridged with an oriented clay deposit. In this condition a current of 220 milliamperes passed thru the system. The deposited Bentonite was then severed with a knife. The current fell immediately to 10 milliamperes. This would seem to indicate that when the clay particles are brought very close together, probably into contact, that there is considerable conductivity which is probably due to ions on the surface. If a film of water of sufficient thickness separates the particles this "ionic chain" is broken and the resistance increases.

The effect of concentration on the conductivity of a series of Miami-clay sols is shown in Fig. 1. These sols were prepared from an H-clay sol purified by prolonged electrodialysis by adding equivalent quantities of the different hydroxides. The maximum concentration secured was not great (3.0%) so that the particles were still separated from each other by relatively thick films of water. The conductivity of the Ba- and H-clays are almost identical, Ca-clay has about twice and the Na-clay five times the conductance of the Ba-clay. The pH values of the H-clay sols are also shown. (Fig. 1, Curve 1.)

An attempt was made to estimate the concentration of Ca and Ba ions in clays saturated with these ions by treating them with equivalent quantities of the soluble salts, sodium oxalate and sodium sulfate which tend to form by double decomposition insoluble salts with the cations of the clay. This reaction is rather unique in that only one of the 4 products of the reaction are soluble in the ordinary sense.

(1) $\text{Ca-clay} + \text{Na}_2\text{C}_2\text{O}_4 \rightleftarrows \text{CaC}_2\text{O}_4 + \text{Na-clay}$
        Colloidal   True solution   Insoluble   Colloidal
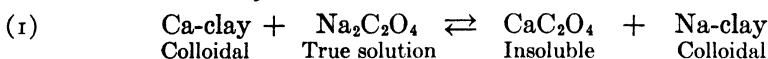
Some idea regarding the extent to which this reaction proceeds toward the right can be obtained from the change in the concentration of the $Na_2C_2O_4$. Ca-clay was treated with an amount of $Na_2C_2O_4$ exactly equivalent to the amount of Ca in the clay. The mixtures were allowed to stand with frequent shakings for over a week for equilibrium to be reached. An aliquot was then freed from clay by passing it thru an ultrafilter using a collodion membrane. The first liquid passing thru the filter was discarded. The ultrafiltrate which is here considered as representing the intermicellar liquid was analyzed for the oxalate ion by titration with 0.01014 N $KMnO_4$. In case of the samples treated with Na_2SO_4 the SO_4 in the ultrafiltrate was determined by conductometric titration with .0500 N barium acetate in 60% alcohol. Very satisfactory endpoints were obtained.
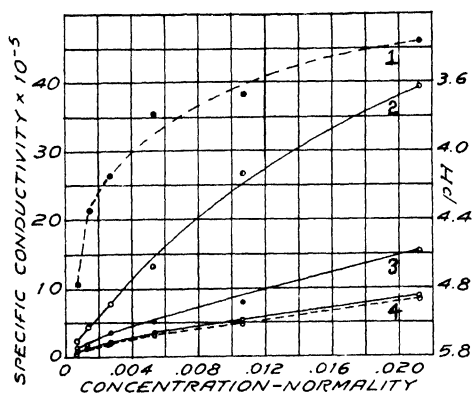
FIG. 1

The specific conductivity of Miami clay saturated with sodium (2), calcium (3), barium (4 solid) and hydrogen (4 dotted). The pH values of the H-clay are shown on curve 1.

TABLE I

The Reaction of Calcium and Barium Clays with Equivalent Quantities of Sodium Oxalate and Sodium Sulfate

Combination	Concentration Equivalents/liter	Specific Conductivity $\times 10^{-4}$	Milli-equivalents insoluble salt formed	Percent of total anion removal
1 Ca-Marion Clay + $Na_2C_2O_4$	.0055	3.49	.28	51.0
2 Ba-Marion Clay + $Na_2C_2O_4$	.0055	5.80	.13	23.6
3 Ba-Marion Clay + Na_2SO_4	.0055	6.80	.20	36.3
4 Ca-Volclay Bentonite + $Na_2C_2O_4$	.0046	3.47	.18	39.5
5 Ba-Volclay Bentonite + $Na_2C_2O_4$	.0046	5.55	.00	0.0
6 Ba-Volclay Bentonite + Na_2SO_4	.0046	2.43	.28	61.2

A summary of the results obtained with two different clay sols is shown in Table 1.

Under the conditions of this experiment 51% of the oxalate added was removed as CaC_2O_4. This would seem to indicate that the concentration of Ca ions supplied by the clay was of the same order of magnitude as that supplied by CaC_2O_4 i.e., 4.24×10^{-5} equivalents per liter. The situation is complicated however by the fact that both substances on the right (Equation 1) are probably less ionized than the original compounds of the same cations. Evidence for this is found in the specific conductivities of the products conconcerned when present in concentrations of .0055 equivalents per liter or saturated in the case they are not soluble enough to reach this concentration.

TABLE II

Specific Conductivity of the Separate Compounds at $25°$ C

Substance	Concentration	$K \times 10^{-5}$
Na-Marion Clay	.0055 N	13.5
Ca-Marion Clay	.0055 N	5.4
Ba-Marion Clay	.0055 N	3.0
H-Marion Clay	.0055 N	3.0
$Na_2C_2O_4$	.0055 N	61.0
Na_2SO_4	.0055 N	63.5
CaC_2O_4	Saturated	1.12
BaC_2O_4	Saturated	8.17
$BaSO_4$	Saturated	.28

While the conductivity of the Na-clay is over twice that of the Ca-clay it is only one-fourth that of the $Na_2C_2O_4$ or Na_2SO_4. This would indicate a tendency for the reaction to proceed toward the right even though an insoluble salt of Ca were not formed. Numerous studies on the base exchange reactions of colloidal clays prove that this is true. The reaction does not proceed as far to the right however in case an insoluble salt of calcium is not formed.

The reaction:

Ba-Marion + $Na_2C_2O_4 \rightleftarrows BaC_2O_4$ + Na-Clay does not proceed as far as in the case of the calcium clay. This is due to (1) the fact that BaC_2O_4 is more soluble than CaC_2O_4 and (2) that Ba-Clay is less ionized than Ca-Clay. The two clays studied differ in their reactions. The amount of Ca^{++} replaced from Ca-Marion by $Na_2C_2O_4$ was greater than the amount of Ba^{++} replaced from Ba-Marion by Na_2SO_4. The reverse was true with the bentonite.

The effect of the concentration of the sodium salt upon the progress of the reaction was studied by means of conductivity measurements. Ca-Marion containing .110 milliequivalents of calcium was treated with increments of $Na_2C_2O_4$ in the ratio shown in Table III. These samples were heated to $90°$ to facilitate the precipitation of the CaC_2O_4 then allowed to stand for a week. The conductivity was measured at $25.00 \pm .05°$ C. The values for the conductivity of the $Na_2C_2O_4$ alone were obtained by interpolation from the values in the International Critical Tables. The conductivity of the pure Na-Clay

and Ca-Clay was known. The above study indicates that about 50% of the Ca was replaced by Na when the ratio of $Na_2C_2O_4$ to Ca was 1. The conductivity curve indicates that the amount of replacement was directly proportional to the concentration of the $Na_2C_2O_4$. The correction due to the changing amounts of Ca- and Na-clays was calculated on the basis of these approximations. The error introduced is apparently quite small. The calcium was practically all removed from the clay by a 50% excess of $Na_2C_2O_4$ above that required for complete precipitation.

TABLE III

Determination of the Amount of Calcium displaced from a Ca-Marion Clay with Increments of $Na_2C_2O_4$ by Conductivity Method

No.	$\dfrac{Na_2C_2O_4}{Ca}$	Normality of $Na_2C_2O_4$	K of $Na_2C_2O_4$ $\times 10^{-5}$	K of Ca$-$clay $+ Na_2C_2O_4$ $\times 10^{-5}$	K due to Na$-$clay$+$ Ca$-$clay$+$ $CaC_2O_4 \times 10^{-5}$
1	0	0	—	4.48	4.48
2	.25	.00275	31.5	16.50	5.9
3	.50	.0055	61.5	24.6	6.5
4	.75	.0082	90.0	34.4	7.1
5	1.00	.0110	119.0	46.8	7.8
6	1.25	.0137	145.0	63.0	8.9
7	1.50	.0165	172.0	73.2	9.6

No.	K due to $Na_2C_2O_4$ $\times 10^{-5}$	Normality of $Na_2C_2O_4$ left	Milliequivalents of CaC_2O_4 formed	Percent of total Ca removed from clay
1	—	—	—	—
2	10.6	.0008	.020	18.1
3	18.1	.0015	.040	36.2
4	27.3	.0023	.059	53.6
5	39.0	.0034	.076	69.0
6	54.1	.0048	.089	81.0
7	63.6	.0057	.108	98.0

The results obtained in a similar study with a Ba-Marion clay treated with $Na_2C_2O_4$ are shown in Table IV. With a 50% excess of $Na_2C_2O_4$ only 54.6% of the Ba is replaced in comparison with 98% in the case of Ca. An interesting difference was noted in the degree of dispersion in the two series. The Ca-clay was highly dispersed with all additions above the 0.5 ratio. No decrease in dispersion was noted even in case of the 50% excess of $Na_2C_2O_4$. This substantiates other observations made in using $Na_2C_2O_4$ as a deflocculating agent in preparing soil samples for mechanical analyses. The amount of dispersion obtained seems to be independent of the concentration of $Na_2C_2O_4$ over a rather wide range. With the Ba-clay however complete flocculation of the clay resulted with all ratios of $Na_2C_2O_4$ to Ba of over 0.5. The higher

concentration of $Na_2C_2O_4$ required to replace the Ba of the clay lowered the charge on the particles more than the resulting replacement of Ba by Na on the particles increased it. MgC_2O_4 is even more soluble than BaC_2O_4. These results indicate that while $Na_2C_2O_4$ is an excellent deflocculating agent for Ca-saturated soils that it might be of no value if the soil were saturated with bases which would tend to form even moderately soluble oxalates.

TABLE IV

Determination of the Amount of Barium displaced from a Ba-Marion Clay with Increments of $Na_2C_2O_4$ by Conductivity Method

No.	$\dfrac{Na_2C_2O_4}{Ca}$	Normality of $Na_2C_2O_4$	K of $Na_2C_2O_4$ $\times 10^{-5}$	K of Ba-clay $+Na_2C_2O_4$ $\times 10^{-5}$	K due to Ca-clay and BaC_2O_4 $\times 10^{-5}$
1	0	0	—	2.71	—
2	.25	.00275	31.5	24.3	11.8
3	.50	.0055	61.5	47.3	12.6
4	.75	.0082	90.0	70.0	13.5
5	1.00	.0110	119.0	96.2	14.2
6	1.25	.0137	145.0	116.8	15.1
7	1.50	.0165	172.0	129.6	15.9

No.	K due to $Na_2C_2O_4$ left in solution $\times 10^{-5}$	Normality of $Na_2C_2O_4$	Milli-equivalents of BaC_2O_4 formed	Percent of total Ba removed from clay
1	—	—	—	—
2	12.5	.0010	.0175	15.9
3	34.7	.0030	.0250	22.7
4	56.5	.0050	.032	29.0
5	82.0	.0075	.035	31.8
6	101.7	.0094	.043	39.0
7	113.7	.0105	.060	54.6

The reaction of Na-Clays with insoluble salts. The fact that only about 50 percent of the Ca was removed from a Ca-Clay by treatment with an equivalent amount of $Na_2C_2O_4$ suggests that a Na-Clay might form an appreciable amount of sodium oxalate if it were treated with the comparatively insoluble CaC_2O_4. At first sight it may seem "rank heresy" to expect substances as insoluble as a Na-Clay and CaC_2O_4 to react to produce a substance as soluble as $Na_2C_2O_4$ in appreciable quantities. It must be remembered however that the other product of the metathesis is Ca-Clay which is much less ionized than Na-Clay. Ungerer[1] has studied this exchange reaction of Na-permutits and clays with certain insoluble phosphates and sulfates and found that with sufficient clay or permutit all of the insoluble phosphate or sulfate could be brought into solution. Reactions of this sort are worthy of

[1] Kolloid-Z., **48**, 237 (1929); **52**, 227 (1930).

further study because they may be of considerable economic significance. It is known as a result of practical field tests that on certain soils the application of different forms of insoluble phosphate fertilizers give just as satisfactory returns as the more soluble forms.

Na-Clay sols (100 cc.) were treated with 0.5 g. of the salts listed in Table V. The salts were prepared by treating the respective bases with a very slight excess of the acids. The precipitate was washed with distilled water by decantation using the centrifuge to accelerate the washings. The mixture was allowed to react for one week. The results shown in Table V indicate that the reaction did not proceed as far as in the experiments in which the clay sols were treated with a soluble salt. It is probable that equilibrium was ap-

TABLE V

The Reaction of Sodium Clays upon Certain Slightly Soluble Salts

Salt 0.500 g. per 100 cc. of clay sol.	Solubility Product	Na-Marion .0055 N 0.768 g. per 100 cc.	
		Milliequivalents of soluble salt formed per g. clay	Percent of Na of clay replaced
1. CaC_2O_4	2.0×10^{-9}	.14	20.0
2. $CaSO_4$	6.1×10^{-5}	.61	100.0
3. BaC_2O_4	1.7×10^{-7}	.30	43.2
4. $BaSO_4$	1.0×10^{-10}	.15	21.5

Salt 0.500 g. per 100 cc. of clay sol..	Solubility Product	Na-Bentonite .0046 N 0.600 g. per 100 cc.	
		Milliequivalents of soluble salt formed per g. clay	Percent of Na of clay replaced
1. CaC_2O_4	2.0×10^{-9}	.11	18.7
2. $CaSO_4$	6.1×10^{-5}	.39	67.0
3. BaC_2O_4	1.7×10^{-7}	.20	33.9
4. $BaSO_4$	1.0×10^{-10}	.084	14.1

proached more closely in the case of these earlier experiments. In the case of the insoluble salts the concentration of all ions involved is very small. The reaction has proceeded far enough however to prove beyond question its significance. If 1 g. of a Na-Clay is capable of bringing into solution the SO_4 in 0.017 of $BaSO_4$, one acre of soil containing 2,000,000 pounds of soil and 200,000 pounds of colloidal clay would on this basis render 3400 pounds of $BaSO_4$ soluble. Even if we consider the reaction in the field only 10 percent as effective as that in the laboratory we still obtain 340 pounds per acre, an amount which compares favorably with ordinary commercial fertilizer applications.

The reaction will probably not proceed so far if the soil is initially saturated with H^+ or Ca^{++}, the cations which predominate in the soils of the humid region. This point is receiving further study.

Further information regarding the concentration of Ca^{++} in a Ca-Bentonite was obtained by a study of the current-voltage curves obtained with the dropping mercury cathode in $N/1000$ $CaCl_2$ solutions and in a Ca-Bentonite sol containing the same total amount of exchangeable calcium. If we assume that at this dilution the $CaCl_2$ is completely dissociated the Ca-Bentonite appears to be only 11.2% dissociated or the concentration of Ca ions is 1.1×10^{-4} which is about one-fourth that of a saturated solution of CaC_2O_4.

The fact that the reaction Ca-Clay $+$ $Na_2C_2O_4$ $\rightleftarrows$ CaC_2O_4 $+$ Na-Clay proceeds only about half way even with the formation of the slightly dissociated Na-Clay favoring the reaction, indicates also that calcium ions are held even more rigidly to the clay particle, than they are to $Ca_2C_2O_4$.

Summary

1. The concentration of cations at the surface of colloidal clay particles is higher than in the intermicellar liquid in a carefully purified system.

2. The concentration of Ca and Ba ions in such purified clays is of about the same order of magnitude as in such insoluble salts as CaC_2O_4 and $BaSO_4$.

3. Clays can decompose these very slightly soluble salts and liberate from them quantities of anions of the same order of magnitude as are supplied in ordinary fertilizer practice.

Department of Soils,
Ohio State University,
Columbus, Ohio.

THE COMPOSITION OF SOIL COLLOIDS IN RELATION TO SOIL CLASSIFICATION

BY HORACE G. BYERS AND M. S. ANDERSON

Introduction

For a period of approximately fifteen years investigators in the Bureau of Chemistry and Soils have been engaged in the accumulation of scientific data concerned with colloid material of the soil. During this period a large volume of accurate information has been secured which has been published in the form of bulletins and journal articles. So far as the Bureau publications are concerned, but little has appeared concerning theoretical aspects of the composition of the colloid. They have concerned themselves, for the most part, | with methods of isolation and estimation, and determination of general ⌐ physical and chemical characteristics.

Meanwhile it is recognized that two more or less clearly defined ideas concerning the character of the colloidal complex have been developed. The one which for some years was dominant, and which, without serious error, may be attributed to van Bemmelen and Stremme, regarded the soil complex as essentially a mixture of three oxides, those of silicon, aluminium and iron. The water and bases of the complex were regarded as held by 'surface' reactions which are not described in terms of the ordinary laws of chemical behavior. The other view, which, of course, is really much older, but submerged for a time by the flood of physico-chemical research, has reappeared, and, indeed, has again become orthodox, though as yet not fully formulated. This view regards the colloid complex as essentially a group of acids, organic and inorganic, which are both weak and unstable, as well as insoluble and essentially amorphous. The salts of these acids, which are the colloid, behave as described by the ordinary laws of chemistry modified by this unusual combination of properties. The essential complex is also in special cases modified by the possible presence of undecomposed minerals and of the *ultimate* products of their hydrolysis. The variants of this view are almost as numerous as the number of contributors to it. In the near future the Bureau of Chemistry and Soils expects to present a discussion of its accumulated data bearing upon this question. Some comments only will appear in the present paper.

In recent years, largely due to the activities of, or stimulated by, the Soil Survey, under the direction of Dr. C. F. Marbut, and based initially upon the investigations of Russian soil workers, there has been developed a system of soil classification dependent upon the properties of the soil profile. This classification takes into consideration, in addition to the dynamic factor of soil development, the parts played also by the parent material in the genesis of the soil. It is the purpose of the present discussion to consider some of our recently accumulated data in their relation to this system of classification and to the composition of the acid complex of the soil.

TABLE I

TABULAR ARRANGEMENTS OF SOIL GROUPS INTO CATEGORIES

Category VII 1. Pedalfers 2. Pedocals

Category VI 1. Podsolic soils 3. Pedocals of Temperate Zone
2. Lateritic soils 4. Pedocals of Tropical Zone

Category V Sub-groups of Group { 1. Chernozem
10 in Category IV 2. Chestnut colored
3. Brown
4. Gray
5. Sub-groups of groups 9, 11 and 12 of Category IV, none of which have yet received distinctive names

Category IV
1. Tundra 9. Northern Temperate Pedocals
2. Podsols 10. Mid-latitude Temperate Pedocals
3. Gray-brown podsolic soils 11. Southern Temperate Pedocals
4. Red soils 12. The various still unknown groups of Tropical Pedocals
5. Yellow soils
6. Prairie soils
7. Laterites
8. Ferruginous laterites

Category III
1. Soils with perfectly developed profiles 3. Soils with perfectly developed profiles
2. Soils with imperfectly developed profiles 4. Soils with imperfectly developed profiles

Category II 1. Soil Series Groups (a very great number) 2. Soil Series Groups (a very great number)

Category I 1. Soil units based on texture of surface horizon Soil units based on texture of surface horizon

Without making a critical historical résumé of the development, from a beginning made by Milton Whitney about forty years ago, of the system of soil classification used in the United States, it may be stated that, while it is the result of a field study of the characteristics of the soil, for many years it was largely confined to a study of the surface, and, to a lesser degree, of

the subsoil. The views of Ramann[1], based largely upon the data of Cushman[2,3] and co-workers in the Bureau of Chemistry and the Office of Public Roads that the weathering of the silicates is "really a result of the hydrolytic action of water," has been accepted, and the work has been greatly influenced by the publication in 1914 of the work of the Russian soil scientists by Glinka.[4] The work of the Soil Survey since 1890, influenced by these results and others, has resulted in the system outlined by Marbut,[5] to be published in the near future. In this system, which was developed through a study of the soils themselves, the influence of environmental factors in producing, and in furnishing explanation of the observed results has been recognized. These factors are chiefly the vegetative conditions which are at the same time determining factors of, and a result of, soil and climate; the climatic conditions, especially of temperature and rainfall; the duration of the soil forming processes; the relation of the terrain to the drainage and to the water table, and the material producing the soil. In this classification, given in Table I, the whole soil profile is considered, Horizon A and its subdivisions, with Horizon B and its subdivisions together constituting what may be considered the solum, or true soil, while the disintegrated parent material is called Horizon C. It is of very considerable interest to discover whether this scheme of classification is reflected by the composition of the soil colloid.

Data and Discussion

Previous to 1924 only a very few chemical analyses of colloid material were available. These were, for the most part, either partial analyses of fine soil fractions or of clays, or were not associated with sufficient field information to permit of any general conclusions.

In 1924 a bulletin by Robinson and Holmes[6] gave the analyses of 44 colloids derived from 19 soil series. On the basis of these analyses the authors drew some very significant conclusions regarding not only the constitution of the soil colloid itself, but also that the molecular ratio of silica to the sesquioxides in a colloid is characteristic of the soil series from which it is derived. They were led to conclude that rainfall is a very important factor in determining colloid composition in that silica is more readily removed by leaching than are the sesquioxides, and high rainfall tends towards the decrease of the ratio. Also since calcium and sodium disappear from soils more readily through leaching than do sesquioxides, therefore the molecular relation of the sum of these bases to the sum of the sesquioxides indicates, by its magnitude, the extent to which leaching has occurred. It follows that, in a general way, these ratios are parallel. In this bulletin, also, the authors call attention

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[1] Ramann: "Bodenkunde" (1911).

[2] A. S. Cushman: The Effect of Water on Rock Powders. U.S.D.A. Bureau of Chemistry, Bulletin 92 (1905).

[3] A. S. Cushman and P. Hubbard: The Decomposition of Feldspars. U.S.D.A. Office of Public Roads, Bulletin 28 (1907).

[4] "Die Typen der Bodenbildung" (1914).

[5] "The Soils of the United States" (1931).

[6] "The Chemical Composition of Soil Colloids," U.S.D.A. Bulletin No. 1311 (1924).

to the relationship between the quantities of silica, alumina and iron oxide required to form the compounds kaolinite and nontronite on the assumption that these exist in the colloid and have the general formula $2H_2O: M_2O_3: 2SO_2$.

Many other investigators have discussed the relation of silica to sesquioxides and of silica to alumina in their relation to the different portions of the soil profile, both in the soil itself and in the colloid fraction. Recently, G. W. Robinson[1] has called attention to variations of the magnitude of the silica-sesquioxide ratio as a result of profile development in Wales. He finds a general tendency toward increase of sesquioxides in the B horizon as compared with the surface soil. These results are in accord with those of Tamm[2] in Sweden, and, indeed, with all investigations of northern humid soils.

The extensive data now available for American soils, most of which have found publication in recent bulletins,[3] render possible a general comparison between the soils and the soil-making processes, and for this purpose the data are presented in full in Tables II and III. In these tables the analytical results have been recalculated in order to better bring out the points under discussion.

In Table II are given the data for soils from both of the main sub-divisions of soils, the Pedocals and the Pedalfers (Marbut's Category 7). The pedocals are represented by the Amarillo silt loam from Texas (Marbut's Category 4) and the Barnes silt loam from South Dakota (Marbut's Category 5). The Pedalfers are represented by three podsols, the Superior fine sandy loam from Wisconsin, the Beckett loam from Massachusetts, and the Emmet fine sandy loam from Michigan. The gray-brown podsolic soils are represented by the Miami silt loam, Chester loams and sandy loams, and Leonardtown silt loams, the mean values of the data for which are given in Table II and the detailed data in Table III. The red soils are represented by the Davidson clay loam from North Carolina, and by the mean values of the Cecil clay loams and sandy clays from Virginia, North Carolina and Georgia, given in Table III. The laterites are represented by the Nipe clay from Cuba, which is a ferruginous laterite. So far as we know, there are no modern truly laterite soils in the United States. The prairie soils are represented by the Marshall silt loam from Nebraska and the Shelby silt loam from Missouri.

In the following discussion the soil making process, so far as its chemical relations are concerned, is considered as essentially one of progressive hydrolysis of the soil minerals. Out of this material the soil development processes, such as translocation or elimination of the products of hydrolytic action and other processes, produce the soil. Translocation of material involves true solution or colloidal suspension, or both. It is recognized, of course, that the hydrolytic process is profoundly influenced by the "catalytic" effect of the presence of carbonic and organic acids and its rate is also a function of the temperature and of the character of the material being acted upon. It is

[1] J. Agr. Sci., 20, 618-39 (1930).
[2] Meddel. Statens Skogsförsöksant (Sweden) 17, 49-300 (1920).
[3] Robinson and Holmes: Loc. cit; Holmes: J. Agr. Research, 36, 459-70 (1930); Holmes and Edington: U.S.D.A. Tech. Bull., 229 (1930); Denison: J. Agr. Research, 40, 469-83 (1930); Anderson and Byers: U.S.D.A. Tech. Bull., 229 (1931).

TABLE II

Chemical Constituents of Colloids from Soils characteristic of Various Soil Groups

Colloids of the Pedocal Group

Location of Profile	Horizon	Depth	Chemical composition calculated on the basis $SiO_2+Al_2O_3+Fe_2O_3=100$			Molecular ratios				Monovalent and divalent bases calculated as milliequivalents per 100 grams					Total base exchange capacity by $BaCl_2$
		inches	SiO_2 per cent	Al_2O_3 per cent	Fe_2O_3 per cent	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca^1 milli-equiv-alents	Mg milli-equiv-alents	K milli-equiv-alents	Na milli-equiv-alents	Total milli-equiv-alents	milli-equiv-alents
Amarillo, Tex.	1	0–5	62.09	27.09	10.82	3.10	3.88	15.19	.255	52.8	103.2	56.9	1.9	220.8	56.6
	2	10–20	62.19	27.42	10.39	3.09	3.85	15.84	.243	56.7	132.0	53.9	0.3	242.9	62.8
	3	30–40	62.43	27.28	10.29	3.13	3.87	16.06	.241	65.4	138.9	53.1	1.9	259.3	63.4
	4	54–64	61.35	28.84	9.81	2.97	3.60	16.57	.217	61.7	140.4	51.4	3.2	256.7	69.2
	5	70–75	62.20	28.56	9.24	3.06	3.68	17.79	.207	75.0	125.5	38.9	1.9	241.3	65.6
	6	96–100	62.97	27.57	9.46	3.18	3.86	17.66	.219	56.4	142.4	48.0	0.3	247.1	70.0
Barnes, S. D.	A_0	0–2½	62.65	23.47	13.88	3.30	4.53	11.93	.379	59.2	47.6	44.8	58.1	209.7	—
	B_2	14–48	60.89	23.85	15.26	3.09	4.32	10.57	.408	46.7	63.0	41.0	45.5	196.2	—
	C_2	60–78	64.00	21.48	14.52	3.55	5.05	10.31	.432	—	—	—	—	—	—

Colloids of Podsol Soils

Location of Profile	Horizon	Depth	SiO_2	Al_2O_3	Fe_2O_3	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca	Mg	K	Na	Total	$BaCl_2$
Superior, Wis.	A_0	0–3	66.44	23.89	9.67	3.76	4.71	18.12	.260	62.1	52.1	16.8	8.4	139.4	78.1
	A_1	3–8	68.52	24.72	6.75	4.01	4.70	26.88	.175	36.1	62.0	45.4	11.0	154.5	56.3
	B	12–30	45.01	35.81	19.18	1.59	2.13	6.20	.343	23.6	84.8	29.1	4.8	142.3	44.0
	C	30–40	55.14	28.77	16.09	2.40	3.24	9.08	.357	21.8	169.2	26.1	1.9	219.0	39.9
Beckett, Mass.	A_0	0–6	52.35	29.64	18.01	2.16	2.99	7.68	.389	23.2	15.4	10.4	8.1	57.1	78.9
	A_1	6–11	59.80	31.56	8.64	2.74	3.22	18.30	.175	14.3	51.1	53.3	7.7	126.4	51.1
	B_1	11–13	28.03	25.15	46.82	0.86	1.88	1.58	1.189	11.4	32.2	17.6	3.9	65.1	—
	B_2	13–24	39.46	36.71	23.83	1.28	1.83	4.39	.416	5.7	58.5	42.0	9.0	115.2	53.7
	C	24–36	46.71	37.50	15.79	1.67	2.11	7.83	.270	6.1	104.2	87.0	8.1	205.1	18.9
Emmet, Mich.	A_1	1–4	61.13	29.26	9.61	2.94	3.55	16.88	.211	19.2	8.9	55.4	23.9	107.4	—
	B_3	24–33	55.33	27.35	17.32	2.45	3.41	8.46	.404	66.0	81.8	56.1	23.2	227.1	—
	C_2	48–60	62.50	19.92	17.58	3.40	5.33	9.41	.566	—	—	—	—	—	—

Colloids of Gray-brown Podsolic Soils

Location of Profile	Horizon	Depth	SiO_2	Al_2O_3	Fe_2O_3	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca	Mg	K	Na	Total	$BaCl_2$
Miami	A_1		58.90	30.01	11.08	2.69	3.33	14.18	.237	27.0	103.5	56.6	7.6	194.7	32.7
Mean values	B		56.76	29.70	13.54	2.50	3.25	11.13	.291	26.3	130.0	72.6	4.8	233.7	38.7
of 9 profiles	C		57.85	29.19	12.97	2.61	3.36	11.72	.284	111.8	156.7	94.9	7.8	350.5	36.3
Leonardtown	A		51.50	34.10	14.40	2.01	2.50	9.62	.268	14.8	44.1	30.2	11.6	100.8	19.7
Mean values of 6 profiles	B		51.19	32.76	16.05	2.01	2.62	8.29	.317	10.4	42.5	26.8	10.6	90.4	22.7

[1] Where analyses show carbonates to be present an equivalent amount of Ca is deducted. In some cases, however, analyses do not include carbonate, which may be present.

TABLE II (Continued)

Chemical Constituents of Colloids from Soils characteristic of Various Soil Groups

Location of Profile	Horizon	Depth inches	Chemical composition calculated on the basis $SiO_2+Al_2O_3+Fe_2O_3=100$			Molecular ratios				Monovalent and divalent bases calculated as milliequivalents per 100 grams					Total base exchange capacity by $BaCl_2$
			SiO_2 per cent	Al_2O_3 per cent	Fe_2O_3 per cent	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca[1] milli-equiv-alents	Mg milli-equiv-alents	K milli-equiv-alents	Na milli-equiv-alents	Total milli-equiv-alents	milli-equiv-alents
Colloids of Gray-brown Podsolic Soils, Continued															
Chester	A		44.65	38.82	16.53	1.54	1.96	7.51	.273	20.5	77.5	20.9	3.5	122.4	25.6
Mean values of	B		46.94	35.39	17.42	1.69	2.26	7.36	.323	13.6	69.9	24.2	3.0	110.6	21.9
8 profiles	C		45.53	38.69	15.77	1.59	2.00	9.06	.271	11.8	46.8	19.0	3.0	80.6	15.3
Colloids of Red Soils															
Davidson, N. C.	A	0–9	43.62	40.67	15.71	1.46	1.82	7.36	.247	20.7	45.6	10.6	1.0	87.9	18.3
	B₁	9–36	43.63	37.43	18.94	1.49	1.97	6.10	.323	20.0	20.3	7.9	trace	48.2	12.6
	B₂	36–60	41.41	34.46	24.13	1.42	2.03	4.54	.448	12.5	17.9	3.8	trace	34.2	15.8
	C	60+	41.44	34.92	23.64	1.40	2.01	4.64	.434	17.8	3.0	3.6	trace	24.4	15.6
Cecil,	A		44.41	43.18	12.42	1.45	1.64	9.75	.184	7.5	22.0	15.0	1.6	45.3	11.6
Mean values for	B		42.02	42.81	15.17	1.38	1.57	7.47	.228	6.0	15.1	8.6	1.9	34.1	8.1
8 profiles	C		42.62	41.91	15.48	1.40	1.63	7.41	.238	4.8	14.5	10.3	2.1	31.7	7.7
Colloids of Laterite Soils															
Nipe, Cuba	1	0–12	11.51	17.89	70.60	0.31	1.09	0.43	2.525	8.2	2.5	trace	trace	10.7	3.1
	2	40–60	6.64	13.72	79.64	0.17	0.81	0.22	3.723	trace	3.5	1.5	0.6	5.6	2.0
	3	100–144	15.28	21.26	63.46	0.42	1.22	0.64	1.915	trace	10.4	3.4	1.0	14.8	2.1
Colloids of Prairie Soils															
Marshall	1	0–14	59.97	28.36	11.67	2.82	3.58	13.14	.263	42.5	99.7	47.3	6.8	196.3	—
	2	14–36	60.07	27.43	12.50	2.87	3.72	12.59	.292	48.5	80.3	44.0	4.8	177.6	—
Shelby	1	0–7	58.35	29.90	11.75	2.64	3.31	12.40	.252	47.1	92.7	25.5	7.1	172.4	—
	2	8–12	57.99	29.81	12.20	2.61	3.30	11.42	.262	46.0	92.8	24.0	6.8	169.6	—
	3	12–20	57.83	29.80	12.36	2.60	3.28	11.18	.265	48.9	100.2	26.8	9.3	175.9	—
	4	20–24	57.56	29.09	13.35	2.60	3.36	10.80	.294	58.2	107.7	28.0	12.3	206.2	—
	5	24–48	58.41	27.75	13.84	2.71	3.57	13.61	.319	77.4	102.7	34.6	14.2	228.9	—
	6	48–60	57.98	27.79	14.23	2.67	3.54	12.72	.328	83.8	102.7	35.2	13.2	234.9	—

[1] Where analyses show carbonates to be present an equivalent amount of Ca is deducted. In some cases, however, analyses do not include carbonate, which may be present.

TABLE III

Chemical Constituents of Colloids characteristic of Various Soil Series

Colloids of the Miami Series

Location of Profile	Horizon	Depth	Chemical composition calculated on the basis SiO₂+Al₂O₃+Fe₂O₃=100			Molecular ratios				Monovalent and divalent basis calculated as milliequivalents per 100 grams					Total base exchange capacity by BaCl₂
			SiO_2	Al_2O_3	Fe_2O_3	$\dfrac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\dfrac{SiO_2}{Al_2O_3}$	$\dfrac{SiO_2}{Fe_2O_3}$	$\dfrac{Fe_2O_3}{Al_2O_3}$	Ca	Mg	K	Na	Total	
		inches	per cent	per cent	per cent					milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	milli-equiv-alents
Eaton Co., Mich.	A	6–10	58.48	30.01	11.51	2.65	3.29	13.46	.245	18.9	121.5	57.5	6.8	204.7	31.7
	B	18–30	57.57	29.04	13.39	2.59	3.36	11.39	.295	28.9	153.3	76.8	8.1	267.1	37.5
	C	34–40	58.29	28.12	13.59	2.68	3.51	11.36	.309	44.6	169.6	85.4	11.0	310.6	42.6
Washtenaw Co., Mich.	A	0–8	59.45	29.76	10.79	2.75	3.39	14.58	.233	33.9	105.7	73.9	11.3	224.8	31.7
	B	8–30	57.29	29.89	12.82	2.55	3.25	11.83	.275	33.2	136.9	97.2	8.4	275.7	33.8
	C	54+	58.57	29.08	12.35	2.69	3.41	12.55	.271	183.7	161.2	100.4	10.6	455.9	23.7
Branch Co., Mich.	A	2–8	60.47	29.84	9.69	2.84	3.43	16.52	.208	7.1	107.6	58.2	8.4	181.3	22.9
	B	9–36	56.59	30.48	12.93	2.48	3.15	11.61	.271	23.5	136.4	90.9	3.2	254.0	33.7
	C	40–60	58.15	29.75	12.10	2.62	3.31	12.72	.260	61.7	155.7	100.4	4.8	322.6	34.3
Miami Co., Ind.	A	4–10	58.37	29.51	12.11	2.66	3.35	12.77	.263	32.8	109.6	55.4	6.8	204.6	29.3
	B	12–20	56.81	29.08	14.11	2.52	3.31	10.66	.310	31.4	142.4	73.3	5.8	252.9	42.5
	A	6–10	59.30	28.84	11.86	2.75	3.49	13.25	.263	34.3	97.7	55.0	4.2	191.2	31.3
	B	15–20	57.01	29.81	13.18	2.53	3.24	11.45	.283	31.4	123.0	60.7	4.5	219.6	40.3
	C	40–50	57.35	29.57	13.08	2.55	3.28	11.62	.282	133.1	154.3	89.2	7.7	384.3	34.2
Blackford Co., Ind.	A	4–7	59.89	30.29	9.82	2.78	3.30	15.92	.207	28.9	120.5	64.3	8.1	221.8	36.8
	B	11–18	56.44	30.37	13.19	2.48	3.15	11.33	.278	27.5	129.0	83.9	4.8	245.2	39.1
	C	38–42	58.14	29.29	12.57	2.64	3.36	11.33	.274	81.0	142.9	102.5	6.5	332.9	32.8
Grant Co., Ind.	A	3–9	61.01	28.85	10.14	2.92	3.58	15.94	.225	32.1	107.1	51.0	6.5	196.7	32.9
	B	10–26	56.58	29.60	13.82	2.37	3.23	10.84	.298	19.3	126.0	69.4	3.2	217.9	37.9
	C	32–42	57.92	28.93	13.15	2.57	3.39	11.66	.290	52.1	147.8	101.1	9.4	310.4	35.2
Hancock Co., Ind.	A	2–12	55.89	32.47	11.64	2.39	2.91	12.71	.229	32.8	58.0	52.7	11.0	154.5	36.5
	B	16–32	55.83	29.54	14.63	2.43	3.30	10.10	.317	25.0	119.1	57.5	2.3	203.9	40.5
	C	36+	56.90	29.28	13.82	2.53	3.30	10.89	.303	53.5	153.3	90.9	5.2	302.9	36.4

TABLE III (Continued)

Chemical Constituents of Colloids characteristic of Various Soil Series

Location of Profile	Horizon	Depth	Chemical composition calculated on the basis $SiO_2+Al_2O_3+Fe_2O_3=100$			Molecular ratios				Monovalent and divalent basis calculated as milliequivalents per 100 grams					Total base exchange capacity by $BaCl_2$
			SiO_2	Al_2O_3	Fe_2O_3	$\dfrac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\dfrac{SiO_2}{Al_2O_3}$	$\dfrac{SiO_2}{Fe_2O_3}$	$\dfrac{Fe_2O_3}{Al_2O_3}$	Ca	Mg	K	Na	Total	
		inches	per cent	per cent	per cent					milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	milli-equiv-alents	mill-equiv-alents
Colloids of the Miami Series, Continued															
Rush Co., Ind.	A	5–14	57.33	30.49	12.18	2.50	3.19	12.45	.256	22.1	104.2	41.8	5.2	173.3	41.1
	B	14–18	56.75	29.48	13.77	2.51	3.27	10.92	.299	16.8	103.7	43.7	3.2	167.4	43.3
	C	60.64	57.45	29.48	13.07	2.57	3.30	11.64	.283	285.4	168.7	89.2	6.8	550.1	51.2
Mean Values	A		58.90	30.01	11.08	2.69	3.33	14.18	.237	27.0	103.5	56.6	7.6	194.7	32.7
	B		56.76	29.70	13.54	2.50	3.25	11.13	.291	26.3	130.0	72.6	4.8	233.7	38.7
	C		57.85	29.19	12.97	2.61	3.36	11.72	.284	111.8	156.7	94.9	7.8	350.5	36.3
Colloids of the Leonardtown Soil Series															
Prince Georges Co., Md.	A	0–7	51.51	33.24	15.25	2.03	2.62	8.95	.293	20.4	52.5	31.0	12.9	116.8	—
	B	7–17	50.86	33.04	16.10	1.99	2.61	8.36	.312	14.3	52.5	27.8	11.6	106.2	—
Prince Georges Co., Md.	A	0–12	49.09	37.26	13.65	1.80	2.21	9.81	.226	8.2	43.7	31.9	13.9	96.7	23.0
	B	12–18	52.14	33.10	14.76	2.07	2.64	9.35	.286	7.5	43.7	28.0	7.7	86.9	23.3
Charles Co., Md.	A	0–7	51.97	33.33	14.70	2.05	2.27	9.36	.282	16.8	44.1	28.5	13.9	103.3	21.0
	B	7–14	51.61	32.58	15.81	2.05	2.69	8.64	.311	12.9	33.7	22.3	11.9	80.8	21.5
	A	0–7	51.28	33.83	14.89	2.03	2.57	9.11	.281	16.1	38.7	28.7	17.4	100.9	18.5
	B	7–14	50.72	33.12	16.16	1.98	2.53	7.24	.305	8.6	37.7	22.1	16.8	85.2	21.5
Prince Georges Co., Md.	A	1–8	53.56	33.35	13.09	2.15	2.72	11.30	.251	11.8	37.7	30.2	3.9	83.6	15.1
	B	8–18	51.41	31.73	16.86	2.05	2.75	8.08	.340	5.0	45.6	30.2	8.4	89.2	23.8
	A	1–8	51.57	33.60	14.83	2.02	2.60	9.20	.283	15.4	48.1	32.1	7.7	103.3	21.1
	B	8–18	50.41	33.00	16.59	1.97	2.59	8.05	.322	14.3	41.7	30.4	7.4	93.8	23.3
Mean Values	A		51.50	34.10	14.40	2.01	2.50	9.62	.268	14.8	44.1	30.2	11.6	100.8	19.7
	B		51.19	32.76	16.05	2.02	2.62	8.29	.317	10.4	42.5	26.8	10.6	90.4	22.7

TABLE III (Continued)

Chemical Constituents of Colloids characteristic of Various Soil Series

Location of Profile	Horizon	Depth inches	Chemical composition calculated on the basis SiO₂+Al₂O₃+Fe₂O₃=100			Molecular ratios				Monovalent and divalent basis calculated as milliequivalents per 100 grams					Total base exchange capacity by BaCl₂
			SiO₂ per cent	Al₂O₃ per cent	Fe₂O₃ per cent	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca milli-equiv-alents	Mg milli-equiv-alents	K milli-equiv-alents	Na milli-equiv-alents	Total milli-equiv-alents	mill-equiv-alents
Colloids of the Chester Series															
Chester Co., Pa.	A	0–9	42.57	37.10	20.33	1.44	1.94	5.52	.352	30.7	140.9	20.0	5.5	197.1	29.9
	B	9–28	40.56	33.84	25.60	1.38	2.03	4.20	.483	12.1	111.6	20.2	1.9	145.8	18.4
	C	40+	43.13	33.46	23.41	1.51	2.19	4.86	.450	14.3	84.3	24.0	2.3	124.9	18.2
Cecil Co., Md.	A	1–8	42.47	39.74	17.79	1.41	1.81	6.32	.287	3.2	120.5	8.7	0.3	132.7	27.7
	B	8–30	47.88	33.96	18.16	1.78	2.39	6.97	.343	3.6	77.9	18.7	0.6	100.6	26.0
	C	42–60	46.96	42.92	10.12	1.61	1.85	12.25	.151	8.6	31.3	8.1	2.3	50.3	18.7
	A	0–9	46.67	40.52	12.81	1.65	1.95	9.63	.203	25.3	82.3	28.7	1.9	138.2	27.9
	B	9–28	46.27	38.53	15.20	1.62	2.03	8.06	.252	13.9	66.0	24.6	4.8	109.3	18.2
	C	28–50	47.35	41.64	11.01	1.64	1.93	11.38	.169	7.5	42.7	21.0	0.6	71.8	14.1
	A	0–7	48.30	37.39	14.31	1.76	2.19	8.92	.246	20.0	74.9	22.9	4.5	122.3	25.2
	B	7–32	50.36	33.25	16.39	1.98	2.57	8.13	.316	15.7	76.9	27.4	3.9	123.9	25.7
	C	44–60	50.36	40.68	8.96	1.84	2.10	14.86	.141	12.8	31.7	13.0	2.6	59.9	15.0
	A	0–10	41.22	43.57	15.21	1.31	1.60	7.16	.224	18.9	68.5	20.0	0.6	108.0	22.5
	B	10–30	45.27	39.58	15.15	1.55	1.94	7.90	.245	12.5	60.0	20.2	0.6	93.3	19.9
Harford Co., Md.	A	1–9	45.60	37.57	16.83	1.60	2.06	7.18	.287	18.6	63.5	22.5	2.9	107.5	19.9
	B	9–28	46.33	35.83	17.84	1.66	2.19	6.87	.319	11.4	34.7	21.7	1.9	69.7	18.1
	C	40–60	41.22	37.26	21.52	1.37	1.87	5.07	.370	11.1	42.2	20.6	5.8	79.7	12.0
Montgomery Co., Md. A	A	0–8	41.81	37.32	20.87	1.40	1.90	5.30	.359	12.8	58.0	17.2	1.6	89.6	22.7
	B	8–34	46.60	33.53	19.87	1.77	2.35	6.22	.379	16.1	68.5	21.2	1.6	107.4	26.9
	C	54+	44.18	36.20	19.62	1.55	2.07	5.96	.347	16.8	48.6	27.2	4.2	96.8	13.5
Montgomery Co., Md. A	A	0–8	48.59	37.36	14.05	1.77	2.20	10.01	.222	34.6	11.4	27.4	10.6	84.0	29.0
	B	8–32	52.27	34.61	13.12	1.79	2.56	10.54	.243	23.2	63.5	39.3	8.4	134.4	22.7
Mean Values	A		44.65	38.82	16.53	1.54	1.96	7.51	.273	20.5	77.5	20.9	3.5	122.4	25.6
	B		46.94	35.39	17.42	1.69	2.26	7.36	.323	13.6	69.9	24.2	3.0	110.6	21.9
	C		45.53	38.69	15.77	1.59	2.00	9.06	.271	11.8	46.8	19.0	3.0	80.6	15.3

TABLE III (Continued)

Chemical Constituents of Colloids characteristic of Various Soil Series

Location of Profile	Horizon	Depth inches	Chemical composition calculated on the basis SiO₂+Al₂O₃+Fe₂O₃=100			Molecular ratios				Monovalent and divalent basis calculated as milliequivalents per 100 grams					Total base exchange capacity by BaCl₂
			SiO₂ per cent	Al₂O₃ per cent	Fe₂O₃ per cent	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	Ca milli-equiv-alents	Mg milli-equiv-alents	K milli-equiv-alents	Na milli-equiv-alents	Total milli-equiv-alents	milli-equiv-alents
Colloids of the Cecil Series															
Goochland Co., Va.	A	0–8	49.07	40.53	10.39	1.77	2.05	12.50	.164	4.3	38.7	17.0	3.6	63.6	9.0
	B	12–30	44.67	41.89	13.44	1.50	1.81	8.80	.205	1.8	25.8	9.8	1.9	59.3	8.3
	C	60+	44.53	39.66	15.81	1.51	1.90	7.45	.255	2.9	27.8	8.9	1.6	41.2	7.6
Rockingham Co., N.C.	A	4–10	44.71	41.34	13.94	1.51	1.83	8.48	.216	7.1	—	21.9	0.6	—	8.0
	B	16–38	44.66	41.49	13.85	1.50	1.82	8.54	.213	5.4	11.9	13.6	0.6	31.5	6.9
	C	70+	43.74	40.73	15.53	1.46	1.82	7.47	.243	1.4	10.4	8.9	1.6	22.3	5.8
Davie Co., N.C.	A	1–8	49.44	40.33	10.23	1.78	2.08	12.81	.162	2.5	20.8	15.5	0.6	39.4	13.7
	B	20–50	45.99	39.69	14.32	1.59	1.96	8.51	.231	11.1	24.8	7.6	0.3	43.8	9.6
	C	50+	45.39	39.38	15.23	1.55	1.95	7.89	.247	11.1	25.3	21.3	0.6	58.3	10.5
Rutherford Co., N.C.	A	0–5	41.78	44.59	13.63	1.33	1.59	8.12	.196	7.9	27.8	7.4	1.9	45.0	9.4
	B	5–36	38.26	44.18	17.56	1.18	1.47	5.77	.254	8.9	6.5	3.8	4.2	23.4	5.6
	C	72–96	36.10	50.13	13.77	1.03	1.21	6.94	.174	8.2	6.9	3.8	2.9	21.8	7.0
Clarke Co., Ga.	A	1–5	42.12	46.21	11.67	1.33	1.54	9.56	.161	7.5	6.5	22.1	0.6	36.7	10.7
	B	5–60	39.92	45.90	14.18	1.35	1.48	7.46	.198	5.0	26.8	10.8	1.0	43.6	7.3
	C	110–130	40.47	41.30	18.23	1.29	1.66	5.87	.282	7.1	25.3	7.9	1.6	41.9	7.2
Wilkes Co., Ga.	A	0–9	41.90	44.50	13.60	1.34	1.34	8.16	.195	11.1	20.3	8.7	3.2	43.3	18.0
	B	9–36	39.72	47.77	12.51	1.20	1.20	8.41	.167	12.5	11.4	7.4	0.3	31.6	12.5
Troup Co., Ga.	A	2–6	44.26	45.19	10.54	1.42	1.55	11.11	.150	8.9	17.9	21.3	0.6	48.7	10.0
	B	20–35	42.14	40.51	17.35	1.39	1.51	6.33	.275	0.7	5.0	9.6	4.8	18.7	6.6
	C	75–90	45.65	42.03	12.32	1.55	1.49	9.79	.188	2.5	2.0	13.6	0.6	18.7	5.7
Chambers Co., Ala.	A	0–7	41.97	42.71	15.32	1.12	1.12	7.24	.230	10.4	22.3	6.4	1.6	40.7	14.0
	B	8–24	40.81	41.08	18.11	1.31	1.31	5.96	.283	2.9	8.9	6.4	2.3	20.5	8.1
	C	25–59	42.43	40.11	17.46	1.40	1.40	6.43	.279	0.7	3.5	7.9	5.5	17.6	10.3
Mean Values	A		44.41	43.18	12.42	1.45	1.64	9.75	.184	7.5	22.0	15.0	1.6	45.3	11.6
	B		42.02	42.81	15.17	1.38	1.57	7.47	.228	6.0	15.1	8.6	1.9	34.1	8.1
	C		42.62	41.91	15.48	1.40	1.63	7.41	.238	4.8	14.5	10.3	2.1	31.7	7.7

also to be kept in mind that the consequences, as well as the degree of dispersion, are modified by the quantity of water entering into the operations, and by the character and quantity of the materials through which percolating waters must pass, as well as by erosional effects both at the surface and within the body of soil and soil material.

From Table II it will be noted that when the analytical data are recalculated so that the sum of the three chief constituents equals 100%, certain marked differences are evident in the different groups. In the pedocals the silica, alumina and iron oxide content is nearly constant. In the case of the Amarillo there are two distinct series of layers, 1 to 3 and 3 to 6. In each a layer is marked by the fundamentally characteristic accumulation of calcium carbonate. In the third stratum the quantity of CO_2 is 0.35%; in the fifth 11.82%.[1] In the soil itself the percentages were not determined. The field data, as collected by the Soil Survey indicate clearly that the lower set of strata represents an old and buried soil and, indeed, this fossil soil had reached a much higher degree of maturity than the present soil. The material from which both were developed is of the same character. These facts make the essential constancy of the colloid composition the more striking and illuminating. The maximum range of silica throughout the profile is 1.62%; of alumina, 1.75%; of iron-oxide, 1.58%. This constancy is also revealed by the molecular ratios of silica to alumina, a range between 3.60 and 3.88; of silica to iron oxide, between 15.19 and 16.57 for the solum, and in the whole profile between 15.19 and 17.99, and of silica sesquioxide between 2.97 and 3.18. This latter value is about fifty per cent greater than is required for the composition of kaolin.

The combined water also is strikingly constant. If we eliminate carbon dioxide loss and the loss due to organic matter and recalculate the data for the Amarillo profile, the range for the first four layers is 8.06, 7.36, 7.90 and 7.76. This constancy of the composition of the colloid of the various horizons is the more remarkable in view of the range of the mechanical composition of the soil.[2] The inorganic colloid content is 23.9% for the first horizon and 42.8% for the second. When we turn to the content of bases in the soil colloid the following relations appear. The magnesium content is high as compared with the other bases, and its constancy in the profile, except in the first horizon, leads to the suspicion of the presence of undecomposed minerals in the colloid, or of the existence of the same definite complex in all horizons, especially when considered along with the like constancy and high content of potassium. The high total base content in comparison with the total base exchange capacity and the total exchangeable base are in accord. The fact that in each horizon the excess of exchangeable base over the total base exchange capacity, as determined by the use of normal barium chloride, accords with the pH values of the whole soil. These values are, for the respective horizons, 6.5, 7.8, 7.8, 7.9 and 8.3.

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[1] Anderson and Byers: U.S.D.A. Tech. Bull., **229** (1931).

[2] Anderson and Byers: Loc. cit.

The same relations shown by the Amarillo profile are also shown by the Barnes profile with such exceptions as are to be expected from the facts that the Barnes soil is developed near the east side of the Chernozem area and therefore under higher rainfall and from calcareous glacial drift instead of calcareous sand and clay. There is a somewhat greater contrast between the C horizon and the A and B in respect to silica-alumina ratio and the silica-sesquioxide ratio. There is also shown by the distinct though slight change of silica alumina ratio, and the very marked alteration of the silica-iron ratio between the A and B horizon, definite indication of a concentration of alumina and of iron-oxide in the B horizon at the expense of the A, a process most marked in the podsol and podsolic soils of the humid regions.

The most interesting difference between these profiles is the difference between the calcium and magnesium content of the A horizon as compared with the B. In general, it may be said that the A horizon is enriched by the ash content of the plants, a part of which is derived from the B horizon. The Barnes profile, with its abundant organic matter, shows this relation for calcium and potassium and a marked decrease in magnesium content, while the Amarillo shows a slight decrease in calcium, and the expected decrease in magnesium and a very slight excess of potassium in the A horizon of the colloid as compared with the B horizon. This analytical difference in the potassium is very slight and probably not real, since the reverse relation is shown by the soil itself. The explanation of these differences is found in the greater rainfall and more luxuriant vegetation of the Barnes compared with the scanty rainfall and light vegetative cover of the Amarillo.

There is revealed in the data so far assembled no evidence of any free sesquioxide in the Amarillo colloid and of but small quantities of free oxide of iron in the Barnes.

The greater concentration of colloid in the B horizon of the Amarillo and the Barnes, as revealed by mechanical analysis, may either be due to colloidal-freshet-erosion from the A horizon into streams, or to eluviation from the A and concentration in the B horizon. If the latter, then the evidence points toward the transfer of the constituents as a whole, and to the existence of definite complexes, acidoids, of the silica with alumina and iron oxide.

The data given in Table II for the podsols offer some interesting contrasts. The podsols have two distinct portions of the A horizon, the surface layer high in organic matter and the highly leached "bleicherde." The A horizons are invariably high in silica and low in alumina and iron oxide, when the major inorganic constituents are alone considered, as compared with the B horizon. The silica-alumina ratio for the colloid of the Superior fine sandy loam is the highest yet noted in our analyses, and in the two other podsols is of the same order of magnitude as in chernozem colloids. The silica-iron ratio is exceedingly high, although quite appreciable quantities of iron compounds are present, both in the soil and colloid. That free hydrated iron oxide is not present in the A horizon is indicated not alone by this ratio but also by the color of the colloid and of the soil. By contrast in the B horizon, the silica sesquioxide ratio is low and in the Beckett profile reaches 0.86 in the B stratum, a value

approaching that of laterites. The silica-alumina ratio is, however, relatively much higher, the minimum being 1.83, which is close to that of true clay.

The silica-iron oxide relations are very illuminating. In every case this ratio is markedly different from that in the A horizon, the maximum variation being 18.30 in the A to 1.58 in the B. It is to be noted that in this comparison the total silica is considered. These facts and the color of the B horizon and its colloids leaves no element of doubt that in the podsols the B horizon represents a zone of enrichment at the expense of transportation of material from the A horizon and that the transportation, so far as *segregation of materials is concerned*, is almost, if not quite, wholly of hydrated oxide of iron. That this is true is also indicated by the relatively small increase in the percentages of colloid material in the A_1 and B_1 horizons. These are for the Becket from 3.9% to 5.8% and from the Superior 1.6 to 4.9. In this connection it may also be mentioned that the B_1 horizon is a zone of greater enrichment than is B_2, a fact which would seem to indicate that the concentration of the colloid is the result of a species of filtration in which suspended colloid, the dispersion or solution of which is favored by the organic matter in the surface, is flocculated, or precipitated, by the higher alkalinity of the subsoil, especially when it is young. (These relationships are not new but have been frequently referred to in studies of the whole soil). When the B horizon is once established as a zone of accumulation it becomes a more effective filter, or may even become impervious.

The quantity of bases present in the colloid of the podsol is notably less than in the chernozem soils and, except in the A_0 horizon, the base holding capacity is also somewhat smaller. In the A_0 horizon the high base holding capacity is increased by the presence of organic matter, this relation being characteristic of organic matter. The base exchange content of the podsols is notably less than in the chernozem and by consequence the degree of saturation. The greater quantity of calcium in the organic layer and the smaller quantity of magnesium occurs in all three soils. The increasing quantities of magnesium in the C horizon point to the presence of unhydrolyzed, or at least, less hydrolyzed minerals in the colloid of this horizon.

We may now turn to a consideration of the gray-brown podsolic soils. We find in Table II the mean of eight profiles of Miami, six A and B horizons of the Leonardtown, and six profiles and two additional A and B horizons of the Chester soils. The details for each soil are given in Table III.

The Miami soils are developed from calcareous glacial drift under deciduous forest cover and under higher temperature and somewhat smaller rainfall than the podsols.

The Leonardtown is developed from the sandy material of the coastal plain and the Chester from gneisses and shale. The Leonardtown and Chester are developed at a much higher mean annual temperature than is the Miami, though also under forest cover, mainly deciduous.

In the Miami series the silica-sesquioxide ratio is much lower than in the pedocal soils and also very much lower than in the A horizons of the podsols, while it is much higher than in the podsol B_1 and B_2. On the other hand, the

silica-alumina ratio is of the same order of magnitude as that of the chernozems. The cause is evident from the silica-iron oxide ratio which is materially and invariably less in the B than in the A. (It is to be noted from the depth measurements that none of the A_0 horizons of the Miami samples were analyzed. These examinations were for a purpose other than that of the present considerations.)

Insofar as podsolization is regarded as a segregation or fractionation of colloidal material, it is evident that the effect is chiefly upon the iron oxide content of the colloids. That eluviation has occurred to a large extent is evident from the fact that in the Miami soils the colloid content of the B horizon[1] is invariably very much greater, from 50% to 400%, than in the A. It is recognized, of course, that this colloid deficiency in the A horizon is due in part to erosion (horizontal elutriation) but it must also be due to eluviation (percolation or perpendicular elutriation).

In the Miami soils the total bases in the B horizon are of the order of magnitude of the pedocals and are somewhat less in the A horizon. The calcium content is undoubtedly greater in the A_0 horizon (not shown in the tables) but the fact is indicated clearly by the complete analyses of Miami soils on file in the Bureau. The total base content of the Miami soils is greater than that of the podsols and less than that of the chernozem, while the total base exchange capacity is less than either. These facts are indicative on the one hand of somewhat greater hydrolysis in the Miami and a considerably more effective leaching. Unfortunately, the base exchange content of these samples was not determined so that the degree of saturation is not available.

When we turn to the Leonardtown series we find a marked decrease in the silica sesquioxide ratio as compared with the series previously discussed, but the silica-alumina ratio is still well above 2 and is less in A horizon than in the B. The podsolic effect is most largely shown by the shifting of the iron oxide. The total base exchange content and the total base exchange capacity are both much less than in the Miami series. These facts are in accord with the general effect to be expected from the greater hydrolysis at higher temperature, and indicate extensive hydrolysis and the elimination of the freed bases and of silica. The strikingly small base exchange capacity in spite of the high silica alumina ratio also points to quartz particles in the colloid, a supposition in harmony with the very large content of silt in the soil which is upwards of 50%.[2] The most striking characteristic of this series is the uniformity of the colloid composition.

The mean values of the colloid from the Chester series are given in Table II. These include six complete profiles and two additional profiles of two horizons given in detail in Table III. In this soil the silica-sesquioxide ratio is well below 2, while the silica-alumina ratio is 1.96 in the A horizon and 2.26 in the B. This is in strong contrast with the reverse relations in the podsols and Miami and the practical absence of such relation in the pedocals. The same difference is shown to a less degree in the Leonardtown series. There is

[1] Holmes and Edington: U.S.D.A. Tech. Bull., **229**, 7 (1930).

[2] Slater and Byers: U.S.D.A. Tech. Bull., **232**, 18 (1931).

not in the Chester series so marked evidence of segregation of iron-oxide, though the increase of the silica-alumina ratio in the B horizon and the decrease of the silica-iron ratio being opposed indicate considerable differentiation. This differentiation is shown by the iron-oxide-alumina ratio which is considerably greater in the B than in the A, as is the case in all the podsols and podsolized profiles. This differentiation in the B horizon is further emphasized by consideration of the mean value of the colloid content, which is 17.6% in the A horizon and 27.6% in the B.[1]

The total bases of the Chester are of the same order of magnitude as those of the Leonardtown series. The mean values are slightly higher but this is due chiefly to one sample from Chester Co., Pennsylvania, in which the magnesium content in the A and B horizon is abnormally great. Mean values of the magnesium content and the greater content in the A horizon as compared with the B would seem to indicate the presence of some partially hydrolyzed magnesium silicate in the colloid. The low base exchange capacity of the colloid indicates a degree of leaching approaching that of the red soils given in the next group. It will be noted that the base exchange capacity of the A horizon is greater than that of the B, owing to the higher base exchange capacity of the organic matter.

Why a similar relation does not appear in the Leonardtown series is not clear since the mean percentages of the organic matter are 7.11% for the Chester (Holmes and Edgington: Tech. Bull., 229, 12) and 7.66% for the Leonardtown (Holmes: J. Agr. Res., 36, 464, (1928)). The explanation in the case of the Miami may be in the fact that the A_0 portion of those profiles, high in organic matter, was not analyzed. Nevertheless, in the A_1 and B in the Miami the organic matter mean values are 5.95% and 1.98% respectively. In these profiles the usual relation of higher base content in the A horizon obtains.

The red soils given in the next section of Table II are the Davidson and the Cecil. The data for the Cecil are the mean values for a series consisting of seven profiles of three horizons and one of only the A and B. The detailed data for these profiles are given in Table III.

The Cecil soils are derived from highly weathered gneiss or schists and the Davidson from diabase, basalt or other quartz free igneous material (Marbut). These two soil series may be described as lateritic, though not yet laterites. The colloid content of the Davidson soil is very high. As determined by the water vapor absorption method it is 27.3, 64.8, 66.5 and 29.6 for the respective horizons given in the table (Anderson and Byers: Bull., 228, 17). The mean values for the Cecils are 11.4 and 42.2% for the A and B horizons. In these soils the silica sesquioxide ratio lies well below the value of two in both soil series, and that of the silica-alumina in the Cecil is also much below two. In the Davidson soil the silica-alumina ratio is well below two in the A horizon and almost exactly two in the B_1, B_2 and C horizons.

Even if we assume that all the iron-oxide exists as free hydrate and that in these colloids there are no free quartz particles or free hydrated silica, it is

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[1] Holmes and Edgington: Bull., 229, 8 (1930).

difficult to avoid the conclusion that free alumina, more or less hydrated, exists in these lateritic soils. In the B horizons the silica-iron ratio in both series is well below that of the A and indicates a distinct segregation by transfer of iron oxide to the B horizon to a greater extent than the corresponding transfer of alumina (podsolization). The same result is indicated by the iron oxide-alumina ratio. This podsolization process is more distinctly marked in the Davidson than in the Cecil profiles. It may be remarked parenthetically that podsolization is a species of natural fractionation of colloid material and that in the near future I. C. Brown of the Bureau will publish the results of his efforts to accomplish the same result by laboratory methods.

In these colloids great extent of leaching is indicated by the very low values of the base content and in particular that of calcium. The extreme degree of hydrolysis is indicated by the low base exchange capacity of the colloids. In both of these respects the weathering has proceeded much farther in the Cecil than in the Davidson soils. In view of the fact that we are dealing here with only one profile of the Davidson and with a very diverse set of Cecil profiles, the above general statement may seem over-bold, but it should be remembered that the work on the Miami, Chester, Leonardtown and Cecil soils indicates a very great degree of constancy in the colloid of a given soil series whatever may be the location of the individual sample provided only that the sample be a fair representative of the series.

When we come to a consideration of the only true laterite we have studied we find the process of hydrolysis and of leaching carried almost to the practical limit. This means the complete conversion of the silicates to alumina and iron oxide and the removal of the bases and also of silica by leaching. In the Nipe soil this is carried to practical completion, the silica-sesquioxide, silica-alumina and the silica-iron oxide ratios all falling to fractional values. Even in this soil the process of podsolization is still detectable in the relation between the silica and iron oxide and between the iron oxide and alumina. Also in this soil the higher value of the silica-alumina ratio, distorted as it is by the material being essentially an iron ore, indicates the reluctant yielding of the alumino-silicates to weathering, a fact also attested by the abundance of clay in the surface of the lithosphere. In this ferruginous laterite the total bases become extremely small and calcium is absent except in the surface layer. The total base holding capacity also becomes an almost vanishingly small quantity.

The Nipe represents, therefore, a soil that has completed its course and is essentially dead, a condition recognized by plants which, on this soil, are scanty and ill nourished. We have no corresponding soils in the United States, so far as the writers are aware. In the Bureau we have analyses of the colloid from a fossil aluminous laterite (Anderson and Byers: Bull., **229**, 17) and of a deep layer from a similar material from Costa Rica (Anderson and Mattson: U.S.D.A. Bull., **1452**, 2) in which the relations are of the same type. In the former the silica sesquioxide ratio is 0.84 and in the latter 0.55. They are not true soils, and are not included in Table II.

We may now, having traced the chemical relationships from West to East and from North to South, return to a consideration of the data contained in the last section of Table II. This section gives the composition of the colloid of the Marshall silt loam from Case County, Nebraska, recalculated from data found in U.S.D.A. Bulletin 1311 (Robinson and Holmes: "The Chemical Composition of Soil Colloids") and of the Shelby silt loam from Bethany, Missouri, recalculated from data soon to be published by C. S. Slater of the Bureau of Chemistry and Soils. These are prairie soils (see Marbut's classification, Table I) and are derived, according to Dr. Marbut, from loessial material in the case of the Marshall and from somewhat calcareous glacial drift in the case of the Shelby. In both soils the dominant vegetation is grass and the temperature and mean rainfall moderate.

The silica-sesquioxide, silica-alumina and silica-iron oxide ratios all show them to be closely related to the chernozem soils. The silica-alumina ratio indicates that hydrolysis has not reached the point where appreciable fractionation of the aluminous silicate has occurred by eluviation. The silica-iron oxide and iron oxide-alumina ratios indicate a certain but limited podsolization. That leaching has proceeded to a very limited degree is clearly indicated by the large values of the basic components and by the very slight concentration of calcium and total bases in the A horizon. The base exchange capacity and the degree of saturation of these colloids have not been accurately determined for the Marshall by methods comparable with those used for the other colloids. The values for the Shelby, however, show that both are essentially saturated soils. The lower horizons of the Shelby profile represent the composition of the glacial drift from which the solum is derived.

The mechanical analysis of the Shelby profile shows about 100% increase in the quantity of colloid in the lower horizons. As determined by the pipette method the percentages are 25.1, 49.6, 46.0, 37.9, 29.8, 31.0, 18.5 and 36.1%, and by the vapor absorption method 23.1, 49.6, 37.2, 27.0, 26.8, 16.5 and 30.6. In this case, then, as in the chernozem soils, the removal of the colloid from the A horizon may be ascribed to horizonal elutriation, erosion, or to eluviation. That the former is effective is evidenced by the character of the streams, especially in freshets, which traverse the prairie soils. That perpendicular erosion, eluviation, also occurs is evident from the data given. If so, it is clear that the transfer is of the colloid as a whole. The conclusion is clear that the colloidal complex in these soils is an essential unit, as contrasted with the colloid of the podsols and of the podsolic soils.

The essential characteristics of the prairie soils as represented by the Marshall and the Shelby series are those of the chernozem, modified by the absence of the zone of carbonate accumulation, due to adequate rainfall for percolation throughout the profile and by incipient podsolization. In these series there is but faint indication of laterization, but in the prairie region the soil surveys show the existence of soil series in which there is no doubt that examination will reveal the evidence of the active operation of this process. The chemical characteristics of the colloids of the prairie soils are in harmony with the high degree of fertility of these soils.

Summary and Conclusions

The striking differences shown by the colloids of the great soil groups given in Category 4 of Table I clearly reflect the field differences upon which the classification is based. The analyses show that the process of podsolization, fractionation of colloids, occurs wherever humid conditions are adequate to permit extensive leaching of the products of soil hydrolysis. They also show that the hydrolytic effects of water are greater, the higher the temperature. It is also clear that not only is the soil making process affected by moisture and temperature, but by the character and quantity of the vegetation upon the soil and that in turn the soil condition is reflected by the character and quantity of the vegetation it will support.

Two rather important inferences from differences between the colloids discussed may be drawn. When soils have but little colloid content it is well known that all attempts to build up a permanent store of available plant food are useless, since percolation rapidly removes the material not used practically at once. Yet such soils are not valueless, as many of the soils of Florida witness. It would appear from the data of Tables II and III that similar attempts with laterites and highly ferruginous soils are almost equally futile. Such soils must be "spoon fed." On the other hand, chernozem, prairie, podsol and podsolitic soils may, if exhausted of their exchangeable base content by over-cropping, be restored to their pristine productivity, provided they be not ruined by erosion, by the proper use of adequate fertilization, or perhaps even by the lapse of adequate time for non-exchangeable bases to become available, and that this renewal is, in a manner of speaking, a permanent restoration.

The other inference requires for its full substantiation a more elaborate discussion and fuller evidence than can be presented in this paper. It is, briefly, as follows: The progressive hydrolysis of the soil forming minerals results *primarily* in the production of an acid complex, probably polybasic, consisting of an alumino-silicic acid radical, in which silica-alumina ratio is greater than two, and in which, as a soil colloid, the acid hydrogen is partially replaced by bases. The salts of this acid, as well as the acid itself, are extremely slightly soluble in water. The details of the structural relations of this acid complex will vary with the structure of its parent material, and with the degree to which iron replaces aluminum in the mineral silicate. The existence of this complex in the colloids of the prairie and podsol soils is rendered extremely probable by the X-ray examinations carried out by Hendricks and Fry[1] and by subsequently obtained, unpublished data, on the Amarillo colloid. In these colloids the X-ray diffraction patterns are those of montmorillonite or ordovician bentonite, the latter term being taken to indicate the presence in the material of quartz. The presence of quartz thus indicated may be considered as due to primary quartz or to silicic acid freed as a result of hydrolysis. As hydrolysis proceeds the alumino-silicate is converted next to a complex having a silica-alumina ratio of two, and, since the iron compounds apparently are more easily hydrolyzable than are the corresponding alumino-

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[1] Soil Science, **28**, 457-479 (1930).

silicates, the colloid complex contains iron chiefly as the hydrated oxide. The hydrolytic influence being favored by time, high temperature and much moisture, eventually produces a complex consisting essentially of hydrated oxides and, with extensive percolation, eventually of those of iron and aluminum alone. At any stage of hydrolysis all of these various compounds may be present and the character of the colloids be dependent upon which stage of hydrolysis is dominant, and to what degree removal of products by water has proceeded.

This conception of the soil colloid necessarily envisages the possible presence, or, better perhaps, probable presence, of colloidal sized particles of quartz and of unhydrolyzed minerals in most colloids.

A soil colloid is, therefore, not to be regarded as a single complex, even if the inorganic portion be considered alone, but as a system not in equilibrium, but proceeding, at a rate determined by environmental conditions, from its birth in the rocks to its ultimate end, a dead soil—the laterite.

Division of Soil Chemistry and Physics,
Soil Investigations,
Bureau of Chemistry and Soils,
Washington, D. C.

WATER RELATIONSHIPS IN COLLOIDS
II. "Bound" Water in Colloids*

BY DAVID R. BRIGGS

There have developed in the last few years several methods by which "bound" water can be determined in a system containing colloids. There are nearly as many definitions of "bound" water as there are methods for determining it. All methods are consistent, however, in that they subject the total water in the system under consideration, to a set of conditions of one type or another which remove or otherwise change the state of a fraction of that water, leaving a portion unaccounted for, this being designated as "bound." The usual idea of "bound" water carries with it the picture of a portion of the water in a system as being associated with the colloid phase with such strength that it is no longer free to exhibit those properties which are characteristic of water, i.e., it is no longer available to act as a solvent, or it cannot be separated from the colloid by freezing or by subjecting the system to pressure, as in an ultrafilter. This water can, however, be removed readily by drying at 100°C. or under vacuum at ordinary temperatures.

Those who have worked with systems containing colloids have repeatedly found that the water contained in the system failed to respond in the usual manner to the conditions to which the system may have been subjected. This generally means that the properties of the water in the system have deviated quite markedly from those characteristic of dilute solutions. Such discrepancies may be explained upon the assumption that a fraction of the water has been removed from the normal state by some type of reaction with the non-water components present, thereby losing its colligative properties. The fraction of water calculated as acting in the normal manner is then designated as "free" water.

But the water thus calculated as "bound" water has not lost its colligative properties, as is evidenced by the fact that it can readily be removed from the system together with the remainder of the water present, when the sample is desiccated in a vacuum at ordinary temperatures. At equilibrium against an atmosphere containing no water vapor (relative vapor pressure equal to zero) all of the water originally contained in the system will be found to have disappeared. That the activity of the "bound" water could be zero when determined by its ability to act as a solvent and still possess a positive value of activity when determined by vapor pressure measurements is obviously a contradiction.

What, then, is "bound" water? Is it possible to give an explanation for these observed discrepancies which will place measurements of "bound" water in colloid systems upon a basis wherein the various methods may be compared and evaluated?

Colloids belonging to the so-called "elastic" gel type give relative vapor pressure-water content curves which show a characteristic S-shape and which are truly reversible so long as no chemical change is brought about in the colloid. The following considerations are confined in their application to this group of colloids, which includes practically all biological colloids.

The relative vapor pressure-water content curve for such a colloid is as true a representation of the relationships existing between the colloid and its associated water as is the corresponding curve for a crystalloid. With the crystalloid this curve approximates closely that required by the laws of dilute solutions wherein equimolecular quantities of solute have the same effect upon the activity of a given amount of the solvent. But with the colloids, no approximation to the laws of dilute solutions is observed. In fact, the forces acting to reduce the activity of the water are not the same in the two cases. With the colloid, this is brought about, at least to a large extent, by the gravitational forces of partial valencies on the surface of the micellae, whereas in the dilute crystalloid solutions the effect is purely kinetic. The relative vapor pressure-water content curve for a colloid cannot be predicted from the laws of dilute solution, nor from any other data which are more easily or accurately attainable than the curve itself. Once having determined the curve for a given colloid, however, it becomes possible to predict the amount of water which will be associated with a given amount of that colloid in any system in which the activity of the water with which it is in equilibrium is known. Provided, of course, that the effects upon the activity of the solvent by the colloid and the crystalloid, or by the various colloid components, are the summation of the effects of the individual components when present alone at the same activity of the solvent, as is the case for crystalloid mixtures.

The object of the experiments described below is to show to what extent the above provision is a fact. Upon this as a basis, an interpretation of some of the various methods being used to determine "bound" water (i.e. the water associated with the colloid) will be made.

Newton and Gortner,[1] as a sequence to their finding that the development of winter hardiness in wheat is accompanied by an increase in the hydrophilic colloid content of the plant, devised a method by which they could measure the "bound" water in plant saps. These investigators pictured this additional ability of the plant to withstand freezing as resulting from changes in the nature of the water which was present in the plant whereby it became less freezable. They argued that, if this were so, it was due to the influence of the colloid which served to remove the water from that condition in which it was freezable, i.e., the colloid had "bound" the water and destroyed its colligative properties. Such a change in the properties of the water should be detectable as a change in its ability to dissolve materials, such as sucrose, the fraction of the water associated with the colloid being considered no longer available to act as a solvent. They therefore sought to measure the amount of water which was thus changed, by measuring the difference between the observed freezing

[1] Bot. Gazette, **74**, 442 (1922).

point depression of a sample of the expressed sap of the plant to which enough sucrose was added to make the solution molar in sucrose, and the calculated value of this freezing point depression if the total water in the sap had been available to dissolve sugar. From the difference in observed and calculated values could be calculated the amount of unavailable water, i.e., the water "bound" by the colloid. The definition which they give for "bound" water then, is that fraction of the water present in the system which is not available to act as a solvent for a crystalloid added to that system. They used a molar solution of sucrose, empirically, and gained very definite differences which were taken to indicate that the colloid was actually holding on to some of the water so tenaciously that the water could no longer act as a solvent for the sucrose.

Hill,[2] using a very accurate type of vapor pressure apparatus, has recently studied the "bound" water content of blood and muscles. His definition for bound and free water is much the same as that of Newton and Gortner, the "free" water present in a system being defined as "the weight of water in one gram of fluid or tissue which can dissolve substances added to it with a normal depression of the vapor pressure"; the definition of Newton and Gortner differs from that of Hill only in that they used "freezing point depression" in place of "vapor pressure depression." Hill's method may be outlined as follows. To determine the water bound by muscle colloids, for example, he weighs a muscle which has been thoroughly soaked and washed with an isotonic Ringer-Locke's solution and then places it in another solution which is twice as concentrated in all components as the original Ringer's solution. The amount of this second solution added to the muscle is such as to contain the same weight of water as is present in the muscle sample. If every non-aqueous component of the muscle possessed an H_2O activity-H_2O content curve which obeyed the laws of dilute solutions the activity depression of the water in the final mixture of muscle plus two-Ringer's solution should equal 1.50 times that in the muscle before bringing it into equilibrium with the final solution. Thus when it is found that the activity depression in the final equilibrium mixture is greater than 1.50 times that of the water in the original muscle before mixing with the two-Ringer's solution, this difference between theoretical and observed values is taken to indicate that a portion of the water in the muscle is bound by the colloid and is unavailable to act as a solvent for the crystalloids contained in the two-Ringer's solution which had been added.

Another and quite different method for measuring "bound" water, which was devised by Rubner[3] and used by Thoenes,[4] has been improved upon in the last few years by Robinson[5] and used to determine the relation of "bound" water to winter hardiness in insects. This method consists, in outline, in freezing the specimen at a temperature of $-20°C$. and then, by calorimetric means, determining the amount of water which has frozen out under these

[2] Hill: Proc. Roy. Soc., **106A**, 477 (1930).

[3] Abhand. preuss. Akad. Wiss., No. 1, page 1 (1922).

[4] Biochem. Z., **157**, 174 (1925).

[5] J. Econ. Entom., **20**, 80 (1927); Colloid Symposium Monograph, **5**, 199 (1927).

conditions. The difference between total and freezable (or "free") water is taken as a measure of the "bound" water in the system. Rubner was interested in the distribution of water in samples of blood and other tissues, and used the temperature, $-20°C.$, as the freezing temperature because he considered that at that temperature all the water which was associated with the salt (NaCl) present in his samples would have been frozen out (although $-23°C.$ is the point at which the eutectic mixture forms) and that any water left unfrozen could be attributed to the influence of the colloids present.

Some other methods for the "bound" water measurement will be mentioned briefly later.

Since we are primarily interested in the amount of water which will be associated with the colloids in a given mixed system, we will define "bound" water in terms of unit mass of the colloid with which it is associated. The definition for "bound" water in a system containing colloid and crystalloid components, then, will be that amount of water which is associated at equilibrium with a unit mass of the colloid component. The amount of water which will be found to be associated with a given colloid must vary with the relative vapor pressure or activity of the water. It therefore becomes necessary when speaking of the "bound" water content of any mixed system to specify the activity of the water in the system at which the "bound" water measurement is made.

Experimental

In working with biological systems, the chief difficulty in the measurement of "bound" water lies in the impossibility, from activity measurements alone, in distinguishing between the relative influences which the various components may be exerting upon the water present. A knowledge of the water activity-water content curve for each component separately is necessary for such a calculation. Then, knowing the activity of the water in the sample, and assuming no reaction to have taken place between the non-water components upon mixing, the water associated with the colloid can be found by reference to its specific curve. But this is not possible with systems which cannot be readily and accurately analysed into their components.

Newton and Gortner, and Hill, have done the next best thing, that of measuring the deviation, between two arbitrary points, of the H_2O activity-H_2O content curve for the system containing the colloid, from that curve which is calculated for the system had it been following the laws of dilute solutions between these points. The results, while making comparisons between samples possible, do not give true values of the total amount of water associated with the colloid at the activity of water at which the measurements are made. Nor do these methods intimate that the value for "bound" water so obtained would vary if the arbitrary points on the curve were changed.

However difficult it may be to get at the true values for "bound" water when working with a complex biological system, it is not difficult to test out the methods so far devised for its determination, to see whether or not they can be interpreted in terms of the theory above outlined. This can be done

by determining the relative vapor pressure-water content curve for a purified (salt-free) colloid and then finding whether or not the values for "bound" water as found by the various methods coincide with values forming points on this curve.

The relative vapor pressure-water content curves for various colloids were determined in a manner described in the first paper of this series wherein the isotenoscope method for measuring vapor pressures of liquids has been used for moist colloids with satisfactory results.

The methods of Newton and Gortner and of Robinson have been followed in making the measurements of "bound" water.

Method of Newton and Gortner

The colloids used in this group of experiments were gum arabic and sodium caseinate. The former was prepared for use by grinding up selected sorts. A sample of this colloid was later electro-dialysed free of ash and found to require 84×10^{-5} equivalents of alkali per gram to neutralize it. The colloid as used thus contained this amount of ionizable calcium and sodium. The sodium caseinate, upon which only one series of determinations was made, served as a check upon the results obtained with the gum arabic. It was prepared from ash-free casein by the addition of 55.5×10^{-5} equivalents of NaOH. This brought the pH of the sample to 6.9. The sample was then dried (not completely) in vacuo at $35°C$. and ground up. It contained no protein hydrolytic products.

In order to obtain their value for "bound" water, Newton and Gortner made use of three freezing point determinations. The first, $\triangle$,was that of the original plant sap or colloid containing solution, the next was $\triangle_o$, the freezing point of this solution after sufficient sucrose had been added to make a molar sucrose solution with the total water present, and the third was $\triangle_c$, the freezing point depression of a molar solution of sucrose in absence of colloid or other non-water compound.

The initial depression, $\triangle$, was taken to be due to the crystalloid components of the sample and was therefore subtracted from the value of $\triangle_o$ in order to eliminate the water held by such crystalloid from the water calculated as "bound" by the colloid. The equation they used to obtain the grams of water bound by the colloid per 1,000 grams of total water was

$$\text{grams} = \frac{(\triangle_o - \triangle) - \triangle_c}{\triangle_o - \triangle} . B$$

where B was the number of grams of water in the molar sucrose solution which was considered free to mix with the remaining solutes in the solution. Sucrose shows an abnormally high molar freezing point depression ($-2.085°C$. in their experiments). The sucrose is supposed to be dissolved in the form of the hexahydrate, thus leaving only 892 grams of the total to act as solvent.

In the calculations made in this paper, B is taken as equal to 1000 in the above equation, because it is considered that the abnormal effect of the sucrose is

taken care of when $\triangle_c$ is subtracted from $(\triangle_o - \triangle)$. At any rate the results so obtained are more nearly in accord with those obtained when alcohol and other crystalloids having normal molar freezing point depressions are used in the place of sucrose in the experiment.

Since crystalloid-free colloids are used in the present experiments (crystalloid ions in salt combination with the colloid are considered as a part of the colloid in these experiments), the initial freezing point, $\triangle$, of the colloid solution, besides being almost negligible, is really due to the colloid or its associated ions and should not be subtracted from $\triangle_o$ because it is desired to obtain values for the entire amount of water associated with the colloid fraction at the various activities of water in the solutions, in order to compare them directly with values obtained by the relative vapor pressure determinations on the colloid.

The equation for calculating the grams of water associated with one gram of dry colloid (per 1000 grams total water) then becomes

$$\text{grams} = \frac{(\triangle_o - \triangle_c) \cdot 1000}{\triangle_o \cdot A}$$

where A = grams of dry colloid per 1000 grams of water, $\triangle_o$ = observed freezing point depression of water in crystalloid-colloid solution, and $\triangle_c$ = freezing-point depression of crystalloid solution of same molar concentration but containing no colloid. (Equals $\triangle_s$ for sucrose and $\triangle_a$ for alcohol in following tables.) The activity of water can be calculated from the freezing point depression according to the following equation,[6]

$$\log a = -0.004211\triangle - 0.0000022\triangle^2$$

where $\triangle$ is the freezing point depression of the solution the activitity, a, of which is desired.

First, a series of experiments was made in order to obtain a comprehensive picture of the effects of mixtures upon the activity of water, especially when one of the components of the mixture was a colloid. Sucrose or ethyl alcohol were used as the crystalloid components of the mixtures. Freezing point determinations were made by the usual procedure, using a Beckmann thermometer and a cooling bath of salt water and ice. The solutions were prepared by adding weighed amounts of the dry crystalloids to a weighed amount of doubly distilled water and then dissolving in this solution a weighed amount of air dry colloid, the water content of which was known. Freezing point determinations were made on this final mixture and upon a solution of the crystalloid in water of exactly the same concentration. The difference in these freezing point depressions was considered as due to the association of a fraction of the water present with the colloid and its associated ions in such a manner that, *at the activity of the water in the solution,* it was not available to act as a solvent for the crystalloid. This amount of water could be calculated as above described. The total water thus held by the colloid divided by the number of grams of air dry colloid present would give the value for the water

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[6] Lewis and Randall: "Thermodynamics," 284 (1923).

in the solution associated with one gram of air dry colloid. To calculate the amount of water associated with one gram of bone dry colloid it was only necessary to use the equation

$$X = (S/B \cdot 100) + C,$$

where X = grams of water bound by 1 gram of bone dry colloid, S = grams of water bound by 1 gram of air dry colloid, as calculated from freezing point depression data, B = bone dry weight of one gram of air dry colloid and C = weight of water in 1 gram of air dry colloid.

The water content of the air dry colloid was determined by drying a sample under vacuum at 60°C. to constant weight.

Freezing Points of Alcohol and Sucrose Solutions and their Mixtures

In Table I are given the freezing point depression data of solutions of sucrose and of ethyl alcohol in water. When these values are plotted against the molalities (a molal solution is taken to signify a solution containing 1 gram mole of solute per 1000 grams of water) it is seen that for alcohol the curve is very nearly a straight line but that the curve for sucrose deviates progressively from a straight line in a manner indicative of a greater apparent degree of hydration of the sucrose molecules at higher concentration, i.e. the sucrose does not attract the H_2O molecule to an extent always equivalent to the formation of a hexahydrate, as has been suggested,[7] but increases in its apparent degree of hydration with decrease in the relative activity of the water in the solution.

TABLE I

Freezing points of sucrose and of ethyl alcohol of various molalities

Molality	0.1	0.2	0.4	0.5	0.8
$\triangle_s$°C.	.189	.380	.765	.975	1.613
$\triangle_a$°C.	—	—	—	.910	1.455

Molality	1.0	1.2	1.5	2.0	3.0
$\triangle_s$°C.	2.050	2.495	3.182	4.336	6.775
$\triangle_a$°C.	1.822	2.183	2.740	3.652	5.420

Abegg[8] showed that the osmotic work performed by a mixtures of solutes dissolved in a given amount of solvent was generally greater than the sum of the osmotic work done by the same amounts of each solute dissolved separately in the same amount of solvent. The freezing point depression for a mixture of solutes would therefore usually be greater than the sum of the freezing point depressions of the same amounts of solutes dissolved separately in an equal amount of solvent. This is probably to be explained by the fact that most solutes when dissolved show a more or less marked solvation effect, and as the solutions become more concentrated (whether by the same or a different solute) the degree of solvation increases. In Table II are given the freezing point data obtained from mixtures of solutions of sucrose and alcohol, together

[7] Scatchard: J. Am. Chem. Soc., **43**, 2406 (1921).
[8] Z. physik. Chem., **15**, 209 (1894).

TABLE II

Freezing point data on mixtures of sucrose and ethyl alcohol in water

Crystalloid added to form designated concentrations in total water

Molality Sucrose	Alcohol	Δ° °C.	$\Delta_s+\Delta_a$ from Table III °C.	$(\Delta_s+\Delta_a) - \Delta^\circ$ °C.	$\dfrac{\Delta_a.1000}{\Delta^\circ} = V_a$ cc.	$\dfrac{\Delta_s.1000}{\Delta^\circ}\ V_s$ cc.	M_a Molar	M_s Molar	$\Delta_a{}'$ extrapolated to $M_a=\Delta_a{}'$ °C.	$\Delta_s{}'$ extrapolated to $M_s=\Delta_s{}'$ °C.	$\Delta_a{}'/\Delta^\circ$	$\Delta_s{}'/\Delta^\circ$
0.2	0.5	1.333	1.290	.043	683	317	.732	.631	1.335	1.255	1.001	.941
0.4	0.5	1.756	1.675	.081	518	482	.965	.830	1.755	1.680	1.000	.956
0.8	0.5	2.644	2.523	.121	344	656	1.452	1.219	2.650	2.538	1.002	.960
1.0	0.5	3.090	2.960	.130	294.5	705.5	1.698	1.418	3.110	2.995	1.006	.969
1.2	0.5	3.555	3.405	.150	256	744	1.954	1.612	3.565	3.441	1.003	.969
1.5	0.5	4.254	4.092	.162	214	786	2.336	1.909	4.253	4.125	1.000	.970
0	0.5	0.910										
0	0.5	0.910										
0.47	0.5	1.910	1.822	.088	477	523	1.048	.882	1.910	1.795	1.000	.940
0.47	0.8	2.412	2.367	.045	603	397	1.327	1.184	2.420	2.455	1.003	1.018
0.47	1.2	3.131	3.095	.036	697	303	1.722	1.552	3.150	3.300	1.006	1.053
0.47	1.5	3.671	3.642	.029	746	254	2.011	1.850	3.672	3.990	1.000	1.087
0.47	0	0.912										

with the amount of water associated with each solute as calculated in the manner used for finding the amount of water associated with colloids as given above.

In this table, V_a and V_s denote the number of grams of water per 1000 grams total water associated with the alcohol and with the sucrose, respectively, as calculated by the equation given above for calculating the fraction associated with the colloids.

In the calculation of V_a, $\triangle_a/\triangle_s$ is used in place of $(\triangle_o - \triangle_s)/\triangle_o$ because the excess in the value $\triangle_o$ over $\triangle_a + \triangle_s$ is due entirely to the sucrose fraction of the mixture. In calculating V_s, $(\triangle_o - \triangle_a)/\triangle_o$ is actually equal to $\triangle_s/\triangle_o$. ($\triangle_a$ and $\triangle_s$ for these calculations are taken from Table I.) These relationships follow from the differences in form of the freezing point-concentration curves of sucrose and alcohol. From these values of V_a and V_s and the number of mols of the corresponding solute known to be present in the mixture, can be calculated the molality of the alcohol and sucrose solutions, M_a and M_s, which would contain these volumes of water. It is then possible to read, by extrapolation of data in Table I, the freezing points of solutions of the crystalloids of these molalities. This value of the freezing point should coincide with that of $\triangle_o$, the observed freezing point of the mixture. The last two columns give values denoting the accuracy with which this extrapolated freezing point coincides with $\triangle_o$. It is to be pointed out that the results of such calculations are almost 100%, the expected value when the calculation is done with the alcohol fraction of the data, but may vary appreciably from the expected value when the sucrose data are used in the calculation. This is due to the difference in the concentration-freezing point depression curves of these two crystalloids. As mentioned before the curve for alcohol is a straight line but that for sucrose is a curve deviating regularly from a straight line. The calculation from sucrose data would therefore require a more complicated equation than that used for the alcohol data in order to acquire the same accuracy. As will be seen later the results upon the gum arabic are more in accord with expected values when an alcohol solution is used as dehydrating agent than when a sucrose solution is used. The reason for this lies in the above explanation.

For solutions of mixtures of crystalloids, however, the amount of solvent which will be found in association with the mixture, at any given activity of the solvent, is the summation of the amounts which would be found associated with equal weights of the individual crystalloids if they alone were dissolved in the solvent at the same solvent activity. It may be assumed that the same will be true when one of the non-solvent components is a colloid. This assumption is substantiated by the following experiments on such mixtures.

"Bound" Water in Colloid Systems from Freezing Point Data

In Table III are shown the results of an experiment designed to find out if the amount of water associated with unit weight of colloid varied radically with the concentration of the colloid (crystalloid content being constant), or if it varied only slightly, as would be expected from the fact that the activity

of the water in the solutions varies very little with the concentration of the colloid. In Table III the total variation in activity of water between solutions containing one to twenty-five grams of gum arabic per one hundred grams of water is shown to be from 0.98022 to .97680 (corresponding to freezing points of −2.061°C. and −2.422°C., respectively). The last column of Table III shows the grams of water in the solutions which are associated with one gram of bone dry gum arabic. These values indicate that the change in water bound by unit weight of the gum arabic, throughout this short range of activity change in the water of the solutions, is very small, possibly within the range of error of the experiment. There is, however, a noticeable tendency toward a lower binding capacity at the lower activities of the water.

Next it was desired to find if the water "bound" by the colloid could be changed by changing the activity of the solution of crystalloid with which it was in equilibrium. To do this it was only necessary to vary the concentration of the crystalloid while allowing the concentration of gum arabic to remain constant. Tables IV and V show the results of this experiment, first

TABLE III

Freezing point data with solutions molar in sucrose and containing varying amounts of air dry gum arabic. (Bone dry weight of arabic = 84.3% of air dry weight)

Grams Arabic per 100 Gm. H$_2$O	Grams Sucrose per 100 Gm. H$_2$O	Δ_0 °C	$\Delta_0 - \Delta_s$ °C.	$\dfrac{\Delta_0 - \Delta_s}{\text{Gm. Arabic}}$	$\dfrac{(\Delta_0 - \Delta_s).100}{\Delta_0 \text{ Gm. Arabic}} = S$	$\dfrac{S}{.843} + .157$
0	34.2	2.045	0	0	0	0
1	34.2	2.061	0.016	.0160	.777	1.079
3	34.2	2.091	0.046	.0153	.734	1.039
5	34.2	2.138	0.093	.0186	.869	1.188
7	34.2	2.160	0.115	.0164	.760	1.058
10	34.2	2.192	0.147	.0147	.671	.963
15	34.2	2.288	0.243	.0162	.708	.997
20	34.2	2.368	0.323	.0162	.683	.968
25	34.2	2.422	0.377	.0151	.623	.896

using sucrose and then using ethyl alcohol as the crystalloid. Table VI gives similar data obtained from solutions containing a constant quantity of Na-caseinate and varying concentrations of ethyl alcohol. In column seven of these tables is shown the total grams of water associated with one gram of bone dry colloid in the solutions. Column eight gives the relative activity of the water present in the solutions as calculated from their freezing point depressions.

The gum arabic used in all these experiments was of the same stock sample. The difference in the water content of the samples of gum arabic used in the sucrose and alcohol experiment was due to the fact that the one used in sucrose experiments was the freshly ground gum while that used in the alcohol experiments had been exposed to the atmosphere for several days after grinding and had taken up some water therefrom. In Table VII and VIII respectively,

TABLE IV

Freezing point data with solutions of varying molality of sucrose and constant gum arabic (air dry) content. (Bone dry arabic = 84.3% air dry weight)

Molality of Sucrose	Grams Arabic (air dry) per 100 grams H_2O	Δ_0 °C.	Δ_s °C.	$\Delta_0 - \Delta_s$ °C.	$\dfrac{(\Delta_0 - \Delta_s).100}{\Delta_0.20} = S$ grams	$\dfrac{S}{0.843} + 0.157$ grams	Activity of Water a
0.6	20	1.388	1.190	0.198	.714	1.004	.9866
1.0	20	2.368	2.050	0.318	.672	.954	.9773
1.2	20	2.788	2.500	0.288	.517	.771	.9733
1.8	20	4.213	3.880	0.333	.395	.625	.9577
2.4	20	5.718	5.315	0.403	.352	.575	.9459
3.0	20	7.240	6.775	0.465	.321	.538	.9322
0	20	0.090	—	—	—	—	—

are given the vapor pressure data on samples of gum arabic and Na-caseinate taken from the same stock samples as those used in obtaining the data in the other tables shown. In these tables the activity of the water present in the colloid samples is taken as equal to the relative vapor pressure exhibited by that water as determined in the isotenoscope.

Fig. 1 shows these values of the activity of the water associated with the gum arabic plotted against the calculated or observed values (from above experiments) of the weight of water associated with one gram of bone dry colloid. It is to be noted that the values as determined from vapor pressure observations form a continuous curve with those calculated from the freezing point data in sucrose
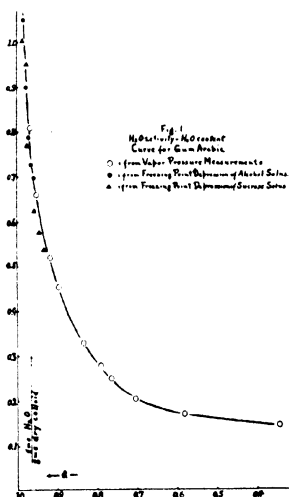
TABLE V

Freezing point data with solutions of varying molality of ethyl alcohol and constant gum arabic (air dry) content. (Bone dry arabic = 87.4% air dry weight)

Molality of Alcohol	Grams Arabic (air dry) per 100 grams H_2O	Δ_0 °C.	Δ_s °C.	$\Delta_0 - \Delta_s$ °C.	$\dfrac{(\Delta_0 - \Delta_s).100}{\Delta_0.20} = S$ grams	$\dfrac{S}{0.874} + 0.126$ grams	Activity of Water a
0.38	20	0.894	0.691	0.203	1.141	1.428	.9914
0.76	20	1.657	1.388	0.269	.813	1.054	.9841
1.14	20	2.403	2.078	0.325	.677	.898	.9769
1.52	20	3.140	2.775	0.365	.582	.789	.9700
1.90	20	3.876	3.465	0.411	.530	.729	.9631
2.28	20	4.616	4.154	0.462	.501	.697	.9562
0	20	0.095	—	—	—	—	—

TABLE VI

Freezing point data with solutions of varying molality of ethyl alcohol and constant content of Na-caseinate of pH 6.9 (containing 55.5×10^{-5} equivalent of Na per gram of casein). (Bone dry caseinate = 92.3% air dry weight)

Molality of Alcohol	Grams Caseinate (air dry) per 100 grams H_2O	Δ_0 °C.	Δ_0 °C.	$\Delta_0 - \Delta_a$ °C.	$\frac{(\Delta_0 - \Delta_a).100}{\Delta_0.20}=S$ grams	$\frac{S}{0.923}+0.077$	Activity of H_2O
.643	20	1.455	1.192	.263	.903	1.056	.9860
.991	20	2.148	1.847	.301	.701	.836	.9794
1.185	20	2.496	2.186	.310	.621	.751	.9761
1.518	20	3.177	2.824	.353	.555	.679	.9701
1.922	20	3.946	3.576	.370	.508	.585	.9624
2.696	20	5.481	5.078	.403	.367	.475	.9481
2.963	20	5.980	5.583	.397	.332	.437	.9434

Fig. 2.
H_2O activity—H_2O content Curve for Na-caseinate
○ :from Vapor Pressure Measurements
● :from Freezing Point Depression of Alcohol Sol'ns
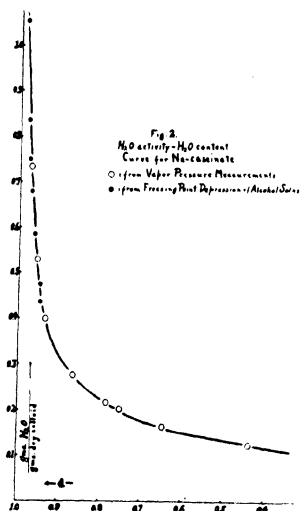
and alcohol solutions. The values obtained in the alcohol solutions seem to be somewhat closer to those determined by vapor pressure measurements than are those obtained in the sucrose solutions. However, all agree very closely, considering the differences in the manner in which the results were obtained. Fig. 2 shows the caseinate data in a similar manner. Here, too, the agreement is very good, verifying the applicability of the theory to quite a different type of colloid.

Theoretically any crystalloid could be used as readily as the two which have been used in these experiments so long as no reactions occurred between it and the colloid. Table IX, however, shows that not all crystalloids may be so used.

Of the eight crystalloids used in this experiment it is found that the values gained with methyl alcohol, acetic acid and glucose compare well with the values obtained when sucrose and ethyl alcohol were used. Gum arabic is the colloid used in these determinations. However, chloral hydrate and acetamide give values somewhat low and sodium and potassium chlorides give values which are very low. It is probable that the electrolytes cause a depressing of the degree of ionization of the gum arabic and that this accounts for the abnormally low value calculated from the freezing point data with these substances. In the case of the non-electrolytes which give low values, it is probable that some sort of physical compound is formed between the crystalloid and colloid which serves to lower the activity of either or both in their effect upon the activity of the water in which they are dissolved. The value ob-

TABLE IX

Freezing point data with solutions of various crystalloids having 20 grams gum arabic content

per 100 grams H$_2$O. (Bone dry weight of arabic = 87.3% air dry weight)

Crystalloid	Molality Crystalloid	Δ_0 °C.	Δ_0 °C.	$\Delta_0 - \Delta_c$ °C.	$\dfrac{(\Delta_0 - \Delta_c).100}{\Delta_0 . 20} = S$ Grams	$S\dfrac{S}{.873} + .127$ Grams	Activity of Water a	Value extrapolated from curves in Fig. 1 Grams
Methyl alcohol	1.312	2.339	2.573	.234	.605	.820	.9754	.850
Glucose. 1H$_2$O	1.000	1.934	2.137	.203	.636	.886	.9795	.925
Chloral hydrate	1.000	1.880	2.033	.153	.501	.701	.9805	.950
Acetamide	1.000	1.935	1.962	.127	.432	.622	.9812	1.000
NaCl	1.000	3.317	3.462	.145	.279	.447	.9670	.760
KCl	1.000	3.159	3.267	.108	.220	.379	.9688	.790
HAc	1.000	1.810	2.001	.191	.636	.886	.9808	.950
Urea	1.000	1.786	1.731	.055	—	—	.9834	—

tained with urea is extraordinarily low. Urea is noted for its peculiar effects in colloid systems. No satisfactory explanation for its action can be offered.

From the results of the above experiments it is quite obvious that the "bound" water cannot be thought of as consisting of a *constant* fraction of the total water.

So long as only one value for the relative activity of the water with which the colloid exists in equilibrium is considered, this concept might be considered as correct. At any other value for the relative activity of the water at which the "bound" fraction may be determined, however, a different value will be obtained for this "bound" fraction. It is always necessary to define the relative activity of the water in the system before it is possible to speak of a definite fraction of it as being associated with or bound to any one of the non-water components. At some definite activity it can be said that the water is distributed according to a certain ratio between the crystalloids or colloids which make up the non-water fraction of the solution. If the H_2O activity-H_2O content curve is a straight line for each and every one of these components as is approximately the case in mixed solutions of crystalloids, then the same ratio will hold at all activities of the water. But if these curves are not straight lines, as is to a small extent the case with crystalloids and as is most radically the case with colloids, then the ratio of the water associated with these non-water components will vary (in case of colloids, radically) with the activity of the water in the system. However, *at any given activity of the water in a*

TABLE VII

Vapor pressure data on gum arabic samples of varying water content

$\dfrac{\text{Grams } H_2O}{\text{Grams dry colloid}}$	Observed vapor Pressure at 25°C. mm. Hg.	Relative vapor pressure or activity of H_2O a
.663	23.33	.950
.810	22.72	.966
.502	21.56	.916
.454	21.05	.895
.329	19.60	.833
.279	18.57	.789
.250	17.95	.763
.203	16.55	.704
.144	8.04	.343
.169	13.65	.581

system in which colloids and crystalloids are in equilibrium, provided the various non-water components have not reacted with each other upon mixing, the amount of water associated with or bound by a given weight of any of the non-water components will always be the same, and it will be the same as that which the given weight of the component will be associated with at the same water activity when it is the only non-water component in equilibrium with water.

The definition of "bound" water offered by Gortner and Newton and by Hill is not complete until the activity of the water in the system upon which the measurement is made is taken into account; the "free" or "bound" fractions of the total water with reference to any non-aqueous component, such as the colloid component, of the system will be found to vary with the activity of the water present in that system.

Hill found that the amount of water which was, according to his definition, "bound" to the colloids present in blood or muscle tissue was of the order of 3% of the total water normally present in those tissues or about 0.1-0.2 grams of water per gram dry solid. This value is quite low when compared with the values which have been obtained from vapor pressure measurements on isoelectric, ash free proteins (see casein in preceding paper of this series) at activities of water comparable to that present in blood or muscles.

Fig. 3 illustrates, in graphic form, the meaning of Hill's measurements in terms of the water activity-water content curve which has been offered in this paper as the theoretical basis upon which the methods used for the determination of "bound" and "free" water in colloid systems may be explained. The same analysis applies exactly to the method of Gortner and Newton. Where *activity depressions* are used in this graphical analysis, Gortner and Newton used *freezing point depressions* and Hill used *vapor pressure depressions*.
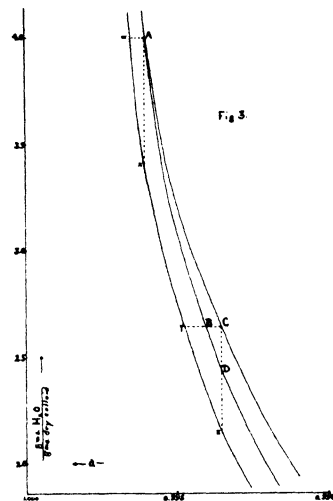
Suppose the curve AC, in Fig. 3, to represent a segment of the true H_2O activity-H_2O content curve for the mixture of crystalloids and colloids present in blood, or muscle, which consists roughly of nineteen parts colloid, one part crystalloid and eighty parts water. Thus the point A would represent the activity of the water in the original tissue or fluid, at which point the water content was equal to four grams per one gram of solid. If, now, at point A on the curve, we could assume that the solids present were all acting as crystalloids and the system was following the laws of dilute solution, we would find that the water activity-water content curve would follow the curve ABD instead of the curve AC. The activity increment BC indicates the extent to which the curve AC has deviated from the laws of dilute solutions between points A and C in the water content of the system. The water content increment CD is a measure of the amount of water present in the system which appears to be not available to the system if it is assumed to be obeying the laws of dilute solution.

The water content corresponding to point D would indicate the "free" water in Hill's or Gortner and Newton's measurements while the increment

CD would measure the "bound" water. Further consideration of the graph shows, however, that these measures of "free" and "bound" water are in no sense absolute. In the first place, the assumption that the entire activity depression corresponding to point A has been brought about according to the laws of dilute solutions is not correct. As a matter of fact, as the water activity-water content curve is followed down from the infinite water content (at which the H_2O activity would equal 1.0) it is found to deviate, from the beginning, from the curve which would be followed were the system obeying strictly the laws of dilute solutions, so that, when a water content of 4 grams per gram of solid is reached, the curve would already have deviated a distance of, say, wA from the dilute solution curve $wxyz$. To measure the water associated with or "bound" to the colloid in the system at any given activity it would be necessary to measure the water content increment lying between the curves AC and $wxyz$ and not between AC and some arbitrary curve as ABD. Of course, we would have to assume, too, that the entire deviation between curves AC and $wxyz$ was due to the colloid present. This is not strictly permissible; some crystalloid solutions deviate likewise to a noticeable extent. But the degree of error arising from such an assumption will be small, by far the greater part of such deviation being due to the colloid present. Thus, at an activity corresponding to point A, the water "bound" by the colloid fraction would be equal to the increment Ax while at activity C, it would equal to Cz. And this water would truly be that "bound" *by the colloid*. It would correspond to the amount "bound" by the isoelectric or ion free colloid, because any ions which might be attached to the colloid would follow the laws of dilute solutions in their relationship with the water present and would thus have no part in causing the deviation observed between curves AC and $wxyz$.

It is obvious that the "bound" water, or better, the water associated with the colloid, as determined by either Gortner and Newton's or Hill's methods will be lower than that which is actually associated with the colloid. Likewise different values could be gained, at the same activity (at point C) of the water present, by conducting the experiment in such a manner that the activity difference between the initial point, A, and the final point, C, was different from the points arbitrarily chosen by these investigators. (In Gortner and Newton's method the point A corresponds to the freezing point of the original plant sap and the point C to the freezing point of the original sap plus enough sucrose to form a molar solution. With Hill's method point A is arbitrarily taken as equal the relative vapor pressure of Ringer's solution while point C corresponds to the relative vapor pressure of approximately a 3/2 Ringer's solution.) And, as pointed out before, the absolute amount of water associated with the colloid will vary with the activity (i.e. with shift in point C) of the water with which it is in equilibrium.

Rubner's Method

The methods used by Gortner and Newton and that of Hill have yielded to a satisfactory explanation in terms of the relative vapor pressure-water content curve of the colloid. But the method described as that devised by

Rubner, and which has been used by Thoenes and Robinson, fails to succumb completely to this explanation.

It is obvious from the above considerations that the activity at which the "bound" water (in this case, the unfrozen water) is being determined by this method is that activity which is equivalent to a freezing point of $-20°C$. This is equal to an activity of water of 0.8221. When equilibrium has been attained at this freezing temperature the water remaining unfrozen must have an activity of 0.8221. By this method no differentiation is made between the water which is associated with the colloid and the crystalloid fractions of the non-water components of the sample. It is therefore of no value for estimating the amount of water which might be associated with the colloid alone. A NaCl solution which freezes at $-20°C$. and exhibits a relative vapor pressure of 0.8221 will be found to contain 3.46 grams of water per gram of salt. If any solution of NaCl is subjected to a temperature of $-20°C$. and the amount of water which does not freeze is determined by the above method, it should be found that for every gram of NaCl in the sample there should remain 3.46 grams of water unfrozen, i.e. "bound" so strongly as to be unremovable under the desiccating force (equivalent to a relative vapor pressure of 0.8221) applied. The same should be true at $-15°C$. except that for

TABLE VIII

Vapor pressure data on Na-caseinate (pH = 6.9) samples of varying water content

Grams H₂O / Grams dry solid	Observed vapor pressure at 25°C. mm. Hg.	Relative vapor pressure or activity of H₂O a
.734	22.90	.974
.530	22.50	.957
.399	22.00	.935
.277	20.35	.865
.216	18.45	.784
.204	17.65	.751
.164	15.20	.647
.124	10.30	.438
.060	4.25	.180

every gram of salt there would be 4.50 grams of water left unfrozen, since $-15°C$. is equivalent to a relative vapor pressure of 0.8636 and a NaCl solution which has this relative vapor pressure contains 4.50 grams of water per gram of the salt. And so at any other freezing temperature to which the solution might be subjected, the amount of water left unfrozen will be such as to form a solution of salt which shows a relative vapor pressure equivalent to that freezing point depression.

An experiment was performed by this method upon NaCl solutions of various concentrations.[1] The amount of water which should be left unfrozen in the solutions, was calculated from the freezing point-concentration data

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[1] The writer is much indebted to Dr. Wm. Robinson for the experimental data reported for this method.

TABLE X

Unfrozen water left in salt solutions of varying concentrations of NaCl when subjected to freezing temperatures $-20°C$. and $-15°C$.

Weight of NaCl in 1 Gm. Soln.	H_2O in 1 Gm. sample	Grams H_2O unfrozen per gram NaCl at $-20°C$.		Obs./Calc. at $-20°C$.	Grams H_2O unfrozen per gram NaCl at $-15°C$.		Obs./Calc. at $-15°C$.
		Calc.	Obs.		Calc.	Obs.	
.005	.995	.0173	.0174	1.006	.0225	.0260	1.155
.009	.991	.0311	.0326	1.048	.0405	.0443	1.093
.017	.983	.0588	.0551	.938	.0765	.0849	1.110
.025	.975	.0865	.1049	1.213	.1125	.1310	1.164

for NaCl obtained from Landoldt-Börnstein's Tables. Table X shows the results as determined at two freezing temperatures, i.e. $-20°C$. and $-15°C$.

The formula used for calculating the frozen "free" water from the calorimetric data is

$$X = \frac{C(T_1-T)-AS(T_o+T)}{80-T_{o/2}}$$

where X = the grams of unfrozen water in sample containing n grams of non-water components,

   C = the heat capacity of the calorimeter,

   A = total weight of wet sample,

   S = specific heat of the wet sample,

   T = final temperature of calorimeter and sample,

   T_1 = initial temperature of calorimeter before adding frozen sample,

   T_o = initial temperature of frozen sample (negative sign disregarded)

If w = the total water present in sample then w minus X = the water left unfrozen or "bound," and $w-X/n$ = the grams of "bound" water per gram of dry solid.

When the fact is considered that these observed results were calculated from calorimetric data obtained in samples (in triplicate) of salt solutions weighing less than a gram, the correlation between the observed and calculated values is very good. This, of course, indicates that the interpretation of "bound" water as measured in this manner is that suggested above, namely it is the amount of water necessary to form a solution with the non-water constituents which will exhibit a relative vapor pressure of 0.8221 or a freezing point depression to $-20°C$.

When samples of colloids were used in place of NaCl solutions, however, the results could not be so simply explained. From their relative vapor pressure-water content curves, the amounts of water which were found to be associated with 1 gram of the dry colloids, at a relative vapor pressure or water activity of 0.8221, were the following:

        Agar (Merck)   0.37 gm.

        Fibrin (crude)   0.33 gm.

        Gelatin (commercial)   0.33 gm.

        Gum Arabic (commercial)   0.32 gm.

        Casein (nach Hammarstein)   0.18 gm.

These are, theoretically, the amounts of water which should remain unfrozen per gram of dry colloid when the sample had been allowed to come to equilibrium at the temperature of $-20°C$. The initial concentration of the colloid in the sample should have no effect upon the amount of water left unfrozen per gram of colloid when this equilibrium has been reached. To what extent the observed values for the water "bound" by the colloids, as determined by this method, differ from the theoretical values given above is shown graphically in Fig. 4, where in the grams of water left unfrozen (or "bound" by one gram of the dry colloid) are plotted against the grams of total water present per gram of dry colloid in the sample.

It seems that the water "bound" per gram of dry colloid increases with dilution and would only approach the theoretical value when the original content of water was equal to the theoretical value, i.e. when no ice would be formed at all. There is little doubt that equilibrium has been attained, since samples left at $-20°C$. for a week or more show no significant difference from those left only 3 or 4 hours.
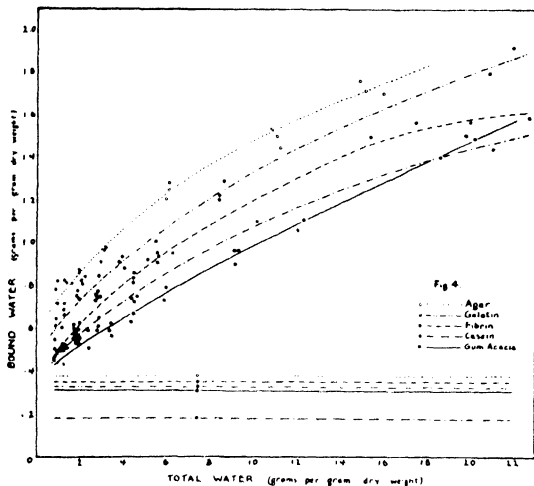
When these unexpected higher values for "bound" water were obtained it was first thought that there might be some heat of imbibition of the colloid as the water which had been frozen out was again allowed to thaw in the presence of the colloid. An analysis of the heat of imbibition-water content curves determined by Katz[9] for several colloids indicated, however, that after the water in the colloid had reached an amount such that it exhibited a relative vapor pressure of 0.8221 (equivalent to a freezing point $-20°C$.) any added water caused almost no preceptible evolution of heat. Actual experiment on gum acacia substantiated this conclusion.

As yet, no explanation for these unexpected values can be given.* It may be due to a protective action of the colloid whereby equilibrium is indefinitely delayed. It may be that the colloid causes formation of microscopic ice crystals to such an extent that interfacial energy relationships would cause

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[9] Kolloidchem. Beihefte, **9**, 1 (1917).

* Note: Data obtained subsequently to the presentation of this paper have failed to substantiate the findings reported for this method and shown graphically in Fig. 4. For gum arabic the curve is found to be a straight line parallel to the horizontal axis but in the region of 0.40 grams H_2O instead of 0.32 grams as required by theory. The method is subject to a large number of errors and it is difficult to make accurate and repeatable determinations, especially when the sample contains a gelatinous material. Since the "bound" water value is always a *small* difference between total and freezable water, all errors of the method are concentrated therein and the percentage variation is quite large.

a shift in the equilibrium point. The fact that the theory holds when measurements are made on crystalloid systems and does not when applied to colloid systems, would seem less to detract from the accuracy of the theoretical picture than to point to some unexpected and unaccounted for influence that the colloid has had upon the formation of ice crystals.

One other method for the determination of bound water may be mentioned and shown to be interpretable in terms of this general picture. Taylor[10] devised a method for estimating bound water in colloids by placing the colloid in a phenol solution of which the temperature was known at which the two phases, water and phenol, separated upon cooling. The colloid would cause a shift in this temperature by an amount bearing a constant relationship to the amount of water which the colloid "bound" or became associated with. It is the same phenomenon which is observed when a colloid is put into a sucrose solution and found to change the freezing point of that solution. The water in the phenol solution will have an activity less than that of pure water and the colloid will be found to have a definite amount of water associated with or "bound" to it at that activity of the water. If it is found that the phenol has had no effect upon the chemical nature of the colloid, the amount of water which the colloid will hold at this particular activity will be the same as it would hold in a sugar solution in which the water shows the same activity, or, that it would be found to contain when mixed alone with water showing a relative vapor pressure of the same value.

Summary

A theoretical basis for "bound" water determinations in colloid systems is outlined in terms of the relative vapor pressure-water content curve (vapor pressure isotherm) of the colloid.

"Bound" water is defined as that portion of the water in a system containing colloid and crystalloid which is associated with the colloid together with those ions which form a part of the colloid complex. "Bound" water is not a fixed quantity of water associated with the colloid but will vary with the activity of the water in the system in a manner consistent with the vapor pressure isotherm of the colloid.

At any given activity of the water in a system in which colloids and crystalloids are in equilibrium, provided the various non-water components have not reacted with each other, the amount of water associated with or "bound" by a given weight of any of the non-water components will always be the same, and it will be the same as that which the given weight of the component will be associated with at the same water activity when it is the only non-water component present in the system.

Some of the methods which have been used for the determination of "bound" water are interpreted in terms of this picture.

Chicago, Illinois.

[10] J. Physiol., **67**, 39 (1929).

FREE AND BOUND WATER IN ELASTIC AND NON-ELASTIC GELS*

BY IVAN D. JONES AND ROSS AIKEN GORTNER

Introduction

The more recent trend in all studies of colloidal systems has been toward an application of physico-chemical methods, in order that the reactions which take place under given conditions may be defined more exactly and be determined quantitatively. Later investigations in the narrow field of studies on the binding of water by substances in the colloidal state have been in keeping with this modern approach to problems in colloid chemistry.

The ability of certain substances in the colloidal state, when in the presence of a given liquid, to hold a quantity of that liquid with great forces of attraction has been long recognized. The exact nature and intensity of these attractive forces have, to date, not been clearly defined.

This attraction, when exhibited toward water, results actually in a hydration of the colloidal particles and gives rise to the phenomenon known as water-binding. Water-binding or hydration is accompanied with certain physical and chemical changes in the colloidal system. Thus, the viscosity is relatively greatly increased, the vapor pressure may be markedly reduced, and a certain portion of the water in the system will no longer act as a solvent.

Foote and Saxton[13,14,15] concluded that a definite portion of water would not freeze from the inorganic hydrogels which they studied and the investigations of Rubner[52] and Robinson[48,49,50] were based on the hypothesis that at temperatures as low as $-20°C$ bound water would not freeze.

It is the purpose of the present paper to report a study of the relation of temperature to the quantities of water which appear to exist in the "free" condition, and in the "bound" or "unfree" condition at known temperatures below the freezing point of a given colloidal system. Also, the behavior upon repeated freezings at low temperatures of certain organic hydrosols and hydrogels is compared with that of certain inorganic colloidal systems.

Historical

Since the early investigations of colloidal systems were generally of a qualitative nature and only in the more recent studies has quantitative technic been introduced, in reviewing the literature dealing with the effects produced on colloidal systems by freezing, we will consider first qualitative and later quantitative observations.

Qualitative studies on the effect of freezing on colloidal systems.—Records are available of observations on the effect of freezing of colloidal substances which antedate the recognition of the phenomena of the colloidal state by Thomas Graham. Thus in 1820 Vogel[63] noted that a distinct change in wheat starch paste occurred upon freezing. When the frozen paste was thawed, a liquid containing but little dissolved substance separated from a spongy mass.

Molisch[36] in 1897 reported a microscopical study of the freezing of a 2% gelatin sol. He found that on freezing, the gelatin formed a net-work, the meshes of the net being filled with ice-masses and air bubbles. Upon thawing the frozen mass, he observed that the gelatin possessed a sponge-like appearance.

Similar studies, upon gum tragacanth, gum arabic, egg albumin, and tannins were made by Molisch.

Bobertag, Feist and Fischer,[2] and Fischer and Bobertag[12] considered that freezing produced, in hydrosols of gelatin, agar-agar, soap, and carragheen moss changes which were only partially or very slowly reversible upon thawing.

Callow,[7] in a study of the rate of ice crystallization through super-cooled gelatin gels, maintained that the "separation of ice irreversibly ruptures the structure of the gel." This conclusion was drawn from observing the behavior of the gels upon repeated freezings.

Inorganic hydrosols have been studied by many workers. The results obtained have not been in complete agreement. Bobertag, Feist and Fischer[2] observed that upon the thawing of ferric hydroxide sols, frozen at $-10°C$ and $-70°C$, the sol was re-formed. Lottermoser[32] observed that this sol, dialyzed until it had a specific conductivity near that of water, was completely precipitated by freezing. He concluded that the electrolyte present in an undialyzed sol served as a stabilizing agent. By the freezing of incompletely dialyzed ferric hydroxide sols, he was able to effect only a partial precipitation of the colloidal material.

Lottermoser and also Bruni[6] independently observed the effect of freezing upon the hydrosol of silicic acid, and reported that upon thawing the frozen sol it separated into a clear liquid and a precipitate.

Vanzetti[62] from repeated experiments with silicic acid gel frozen at temperatures as low as $-200°C$ concluded that the final composition of the gel was independent of the temperature of freezing. A certain portion of the water present could not be removed by freezing.

Liesegang[30] repeated Molisch's experiment with a 2% gelatin sol and reported very different results. He found that the water on freezing formed fernlike ice patterns. On thawing, the patterns remained in finest details, and he adds that the most gelatin was found where the most ice had appeared. Apparently, therefore, water was not separated from the gelatin upon freezing and subsequent thawing. Stiles[56] has raised the question as to whether the differences in results obtained by Molisch and by Liesegang were not caused by different rates of freezing of the gelatin sol.

In an excellent treatment of the fundamental physical and chemical principles of the freezing process Stiles[56] has definitely shown that the conditions under which freezing takes place determine, to a very large degree, the effects which will be produced by freezing. His work was based on the early investigations of Tammann[59] who concluded that in the crystallization of a super-cooled liquid, two factors were important, (A) velocity of crystallization and (B) the number of centers from which crystallization takes place.

Moran[37] in microscopical studies of the effect of freezing on gelatin gels, found that the structures produced in the gel depended upon the rate of freezing and the concentration of the gel. It is of particular interest that Moran demonstrated that centers of crystallization could be either external or internal, this condition being determined by the temperature at which freezing began. Hardy[21] carried on further microscopical investigations with frozen gelatin gels, and states "so far as my observations go, when crystals (internal) of pure ice melt, the water is reabsorbed at once by the surrounding gel, leaving only a tiny cleft."

These studies of Stiles, Moran, and Hardy offer an explanation of Liesegang's observations which were at variance with the earlier studies of Molisch.

Hardy[19,20] advanced the theory that with gels or sols, dehydration could be considered a reversible process, if a gel or sol resulted normally from the addition of a colloidal substance to water; and that it would be an irreversible process, if special conditions were required to produce the gel or sol. Fischer[11] in 1911 pointed out that the freezing process might similarly be considered as either reversible or irreversible, since freezing is only a special type of dehydration.

Quantitative Studies on the Effect of Freezing on Colloidal Systems.—Müller-Thurgau[38] in 1880 published the results of investigations on apple and potato tissue. In his studies the material was first frozen in an ice and salt bath and then introduced into a water calorimeter. From the quantity of heat required to melt the ice in the sample, he was able to calculate the quantity of water which had been frozen. As has been noted by A. Kuhn,[29] Müller-Thurgau's first results were undoubtedly erroneous, for he gave no consideration to the molecularly dissolved substances in his samples. The principle involved in Müller-Thurgau's studies has, however, been of great value in that it laid the foundation for much biological research.

Foote and Saxton[13,14,15] introduced dilatometric technic into studies of the freezing of colloids. They chose as systems for investigations, the inorganic gels of silica, alumina, colloidal ferric hydroxide, and a mixture of lampblack and water. With every system studied they found that a certain portion of the water present remained unfrozen. They accordingly concluded that water in the inorganic hydrogels existed in three forms: (A). Free water—the water which froze between the temperatures 0°C and −6°C. (B). Capillary water—that portion of the water in the sample which froze at temperatures below −6°C. (C). Combined water—the portion of the water which represented the difference between the total water in the sample and the water which could be frozen.

Applications of the dilatometer method have been made by several investigators, notably by Bouyoucos[3,4] in soil studies, McCool and Millar[33] in soil and plant relationships, and by Rosa,[51] and Lott[31] in winter-hardiness studies.

Parker,[45] in 1921, reported some exceedingly important observations on the effect of finely divided insoluble material on the freezing point of different liquids. He found that with water the magnitude of the freezing point depression depends upon at least two factors, (1) the relative surface area of the solid, or the degree of subdivision of the material and (2) the affinity which exists between solid material and water.

Newton and Gortner[43] in 1922 suggested a new method for the quantitative measurement of water held in the "unfree" or bound condition in sols of hydrophilic colloids. This method is based on the hypothesis that a certain portion of the water in a hydrophilic sol is associated with the colloid in such a form that it will no longer act as a solvent, as contrasted with "free" water. The addition, then, of a definite quantity of a soluble material to a sample containing a known amount of water would cause a lowering of the freezing point of the mixture, in proportion to the molar concentration which resulted, and a positive deviation of the observed from the theoretical freezing point depression would be a measure of the bound-water which was present. Kruyt and Winkler[28] have verified the findings of Newton and Gortner regarding the effect of the presence of hydrophilic colloids on the freezing point depression of solutions of molecularly dissolved substances.

The Newton-Gortner method has served as a quantitative measure of bound-water in many plant investigational projects and related studies, e.g. Newton,[39,40,41] Harris et al,[22] Newton and Cook,[42] Newton and Martin,[44] Martin,[35] and Crist.[8]

Kuhn[29] cites an extensive study made by Rubner of water-binding in Laminaria and materials of animal origin. Rubner[52] employed a method very similar to that first used by Müller-Thurgau, and considered the latent heat of fusion of ice to be a measure of the quantity of water which could be frozen. Thoenes'[60] studies on the effect of freezing upon water-binding in gels and animal tissues involved an experimental procedure modeled closely after that of Rubner.

Thoenes concluded that the method yielded reproducible values when dealing with animal tissues but that these values were only relative. It gave a measure of water-binding intensity but not a true measure of the quantity of water which existed in the bound form in the living organism.

Robinson,[48] in a study of winter-hardiness in insects, employed the method described by Thoenes. He improved the technic[49] and pointed out that this method yields only minimal values for bound-water. He demonstrated in a striking manner the importance of bound-water studies in animal physiology.

Moran[37] made quantitative investigations on the effect produced by freezing gelatin gels at different temperatures. Having noted that ice formation was entirely external under certain conditions of freezing, Moran

took advantage of the fact that the ice appearing in such manner could be removed from the resulting partially dehydrated gel sample, and thereby he determined the phase equilibrium between ice and gel at different temperatures. He found the equilibrium completely reversible in the gel concentrations which he studied.

Hill,[23] and Hill and Kupalov[24] have recently studied the bound-water problem in animal tissues using the vapor pressure method. They arrive at results which are not in agreement with those reported by Thoenes,[60] who found relatively large amounts of bound-water to be associated with the hydrophilic colloids of muscle, whereas Hill finds very little if any bound water in either blood or muscle. It seems probable that this finding may in part be explained by the technic used and by the assumptions which Hill made. Since Briggs[5] is presenting on this same program an extensive study of the vapor-pressure method, the reader is referred to his paper for a discussion as to the possible causes of the divergent conclusions noted above. That the majority of physiologists, physicists and physical chemists agree that some sort of water binding occurs in hydrophilic colloid systems is indicated by the extended discussion which was provoked following the recent presentation before the Faraday Society of a summarizing paper on "bound" water by Gortner.[18]

Experimental

The Problem.—It is apparent from the preceding historical review that there is not complete agreement as to the effects which are produced when colloidal systems are frozen.

Similar lack of agreement is found when dealing with methods of measurement of bound water. Freezing of colloidal systems has been employed by some investigators as a method in studying the water-binding in certain materials. Foote and Saxton,[13,14,15] Rubner,[52] and Robinson[48,49,50] considered the freezing method as a quantitative measure of water-binding capacity in the materials under investigation. Thoenes[60] concluded from a study made by means of the Rubner method that it did not give absolute values for water-binding capacity. Kuhn[29] has emphasized, in a very complete review of water binding in colloids, that freezing reduces water-binding in colloidal systems, also, that any freezing method is reliable only to the extent that it measures the intensity with which water is bound, and, accordingly, can not be considered a quantitative measure of water-binding capacity.

Gortner[17] (p. 227 *et seq*), in a general discussion of the problem, suggests that the bound water is probably present in the form of oriented dipoles and adds[18] that, "I do not believe there is any sharp line of demarcation between "free" water and "bound" water, but that we must postulate an insensible gradation between molecules of water having the normal activity of pure water and molecules of water where this activity has been so reduced that such molecules have become to all intents and purposes a part of the solid upon which they are adsorbed. One method of measurement may be sensitive enough to differentiate between water molecules having a given activity and those molecules having a greater activity. Another method of measurement

may give somewhat different results because it draws the dividing line at different activity values. What we in biochemistry need at the present time are extensive series of measurements carried out on many biocolloid systems by many different techniques. When these data have all been accumulated, then perhaps it will be time enough to attempt to theorize as to the exact nature of "bound" water."

The purpose of the present paper was to determine with certainty whether or not "bound-water" would freeze, and if so, at what temperature this freezing would take place. If bound-water would not freeze, this process could be employed as a quantitative measure of the bound-water content of hydrophilic colloidal systems. If bound-water would freeze, it was considered that a relationship should exist between the rupture of the gel structure and the freezing of bound-water.

Newton and Martin,[44] employing the Newton-Gortner method of bound-water measurement with different concentrations of organic hydrosols, found that with increasing concentration of the colloid, there was an increase in the quantity of water which was "bound." This is taken as evidence to support the supposition that gel formation results when the bound-water represents an appreciable portion of the total water present. If then, the bound-water content can be reduced by freezing, a partial or complete rupture of the characteristic gel structure exhibited by certain colloidal systems should result.

The Method.—In order to observe the behavior of hydrophilic colloidal systems upon freezing, it was desirable to employ a method which would permit continuous readings to be taken on a given sample at any desired temperature. Such a method should permit a study of the behavior of the system as the temperature was lowered below its freezing point and also as the temperature was raised again to the melting point of the ice. The dilatometer method was accordingly chosen.

The principle of the dilatometer method is well known and may be summarized as follows:

In any given system changes in temperature are accompanied by corresponding density changes of the system. If with a temperature change, there occurs a liquid ⇆ solid transition, this is, in general, accompanied by a corresponding change in density. If the mass of the system be fixed, the density changes may be followed by the volume changes which occur.

With water, solidification takes place at o°C with a density change[25] from 0.9999 to 0.9168. This density change results in a volume increase of 0.09074 cc. per gram of water.

Therefore, by measuring the expansion produced by freezing, it is possible to calculate the quantity of water which was frozen. If freezing occurs gradually as the temperature is lowered, there will occur simultaneously (A) an expansion resulting from the gradual formation of ice and (B) a contraction resulting from the temperature lowering of the entire system. Knowing the density change for all solids and liquids in the system for any given temperature change, the ice formation which results from a given temperature change can be calculated.

As has been indicated, other workers have used dilatometric technic in studying ice formation in colloidal systems. They have, in general, calculated the amount of water in the system from a moisture determination of the sample under investigation. In addition the quantity of water which was frozen at a given temperature has, in general, been calculated directly from the expansion which resulted from the freezing process.

In the greater part of this investigation, a known quantity of pure water was pipetted into the dilatometer, and the volume change produced by cooling the system to definitely recorded low temperatures was measured. Following the determination of such "water curves" the same quantity of water was added to small amounts of the solid material under investigation in the dilatometer, and the expansion and contraction resulting from exposures to low temperatures were again measured. Thus, in the second series of measurements the conditions were identical with those prevailing in the first, the only difference in the system being the small quantity of material under observation. It was therefore assumed that the two resulting curves were directly comparable, and if the material did not have the ability to "bind" water, that the second curve would coincide exactly with the first one. Further, it was considered that the measure of the quantity of the water which the material would bind would be indicated by the extent to which the two curves deviated from each other. It was expected that gradually lowering the temperature would cause a convergence of the curve resulting from the freezing of the colloidal system toward the curve for pure water. If such convergence did not occur, then one could rightly assume that decreasing temperatures did not alter the amount of bound water. Stated differently, if at the point of initial freezing all water which would freeze was transformed into ice, then the curves resulting from plotting the readings obtained at different temperatures below that of freezing would be a line parallel to that given by the pure water sample. Any deviation from such a parallel line would be expected to take place in the direction of the pure water line, as it would thereby indicate a decrease in the total quantity of water held in the non-frozen state.

FIG. 1
The dilatometer as used in this study.

Description and calibration of the apparatus.—The apparatus consisted of a bulb-capillary-stem dilatometer mounted on an engraved meter stick as shown in Fig. 1, and a low temperature thermostat in which the desired low temperature could be produced and maintained.

The dilatometer figured was the most satisfactory and most sensitive one of many designed for these studies. The bulb of the instrument was blown from pyrex tubing about 0.5 × 3 cm. One end was sealed shut; the other end was fitted with a carefully ground glass stopper which was held firmly in place by means of rubber bands. The stem about 55 cm. long was of pyrex capillary tubing having a 1 mm. bore and was attached to the center of the bulb at a direction perpendicular to its long dimension.

The dilatometer had a capacity of about 5 cc. The sample taken usually occupied a volume of from 1 to 3 cc. The remainder of volume of the dilatometer bulb and a portion of the stem were filled with pure toluene.

Toluene was chosen because of its known coefficient of thermal expansion,[25] its high boiling point, and its inactivity toward aqueous colloidal systems. The high coefficient of thermal expansion of toluene produced a decided density change with a small temperature change, therefore serving to counterbalance the expansion produced by the freezing of the water in the sample and made possible the use of a relatively short stem for the dilatometer.

The stem of the dilatometer was attached perpendicularly to the bulb primarily to avoid a possible fracture of the bulb resulting from the expansion of the sample when it froze, and also to facilitate the filling the dilatometer, mixing the sample, and freeing the system from air bubbles.

The volume of the dilatometer was calibrated at room temperature by means of weighing the mercury it would contain. The diameter of the capillary stem and the uniformity of its bore were determined by measuring with a microscope equipped with a movable stage the length of a weighed mercury thread in consecutive sections of the tube. All variations in the bore of the selected capillary were found to be well within the limits of experimental error. The actual diameter of the uniform capillary was further checked by weighing a thread of mercury which filled the greater portion of the length of the tube. The capillary chosen had a volume of 0.0096078 cc. per cm. length.

It was possible to read the length of the toluene column in the capillary with an accuracy of 0.05 cm., thus permitting an accurate measurement of a volume change as small as 0.00048 cc.

The low temperature thermostat consisted of a well-insulated double-walled container, the inner vessel having a capacity of approximately 1 liter. The cooling medium was alcohol, the temperature of which was lowered as desired, by adding a sufficient amount of solid carbon dioxide, similar to the technic suggested by Dunn.[9] In order to assure uniformity of temperature in the bath the alcohol was stirred continuously by a small electric motor. It was essential to maintain a uniform temperature in the bath, since the temperature of the bath was taken to be the temperature of the system inside the dilatometer after the contents of the dilatometer had arrived at a temperature equilibrium. The size and construction of the dilatometer prohibited the use of a thermometer inside of this instrument.

A 0°C to −65°C pentane thermometer was used in determining the temperatures. This thermometer was checked against a thermometer which had been standardized from a Bureau of Standards certified instrument.

Materials. The materials employed in this investigation fall into two classes. (A) those substances which form gels of the elastic type and (B) those which form inelastic gels.

Gelatin was chosen as a typical substance which forms an elastic gel. Gelatin was especially suitable from many standpoints, two of the factors being its behavior in cold water and its ready sol ⇋ gel transformation.

Since the method of mixing water with the dry sample was that of adding a definite and constant quantity of water to the dry material in the dilatometer, it was essential that the finely divided substance should be readily wetted in a uniform manner. Gelatin behaves satisfactorily when placed in cold water but most other dry hydrophilic substances tend to form a lump, the interior of which is only very slowly wetted.

After the initial swelling of the gelatin in cold water had taken place, the dilatometer could be immersed in warm water, this causing the formation of a sol which upon cooling would set to a gel.

The other substance chosen as an example of the elastic gel type was the thick portion of the white from fresh eggs.

Materials of the inelastic-gel type were activated silica gel obtained from the Silica Gel Corporation, and the colloidal coagulum of ferric hydroxide.

Experimental Data

The Volume Change of Toluene with Temperature.—In order to test the accuracy of the dilatometer, a study was made of the behavior of pure toluene upon exposure to temperature changes. The dilatometer was completely filled with toluene, and the readings taken at different temperatures were plotted. The resulting curve is shown in Fig. 2. All readings fell on a straight line and the values were easily reproduced in repeated temperature-lowering or temperature-raising cycles. When this line was checked against the existing data on the contraction of toluene[25] our values proved to be about 2.5% too high. No reason was found for this discrepancy. Table I gives the readings from which the toluene curve was constructed.

In recording the data taken in these studies, it was considered, in every case, that the toluene column had zero length when the system was in equilibrium at 0°C. Therefore the readings which resulted from temperature-lowering are recorded as cm. contraction or as a negative length of the toluene column. If then at any temperature an expansion occurred which caused the toluene column to rise above the point at which it stood at 0°C, the readings became positive in sign. It will be seen that this change in sign of toluene length occurred in every case where water was frozen.

The Volume Change of the System, Toluene-Water, with Temperature Change.—Fig. 2 shows the form of the curve which results from freezing a sample of pure water. In this instance 1.955 grams of distilled water was frozen. The line AB represents the contraction of the toluene-water system between the temperatures 0° C and −11.1° C; line BC represents the elongation of the toluene column in the capillary stem of the dilatometer due to expansion of the system produced by separation of ice at a constant temperature; line CD then represents the contraction of the system, toluene-ice. It will be observed that the curve resulting from the freezing of the water sample is well represented by a straight line, as is indicated by readings taken both during temperature-lowering and temperature-raising.

Fig. 2 represents but one of many determinations, all of which were in exceedingly close agreement. Accordingly, the curves of Fig. 2 have been used as reference curves in later studies.

In most of the experiments undertaken a constant quantity of water was used, the variable factor being different materials under investigation of varying dry weights of samples of such materials mixed with the given weight of water.

FIG. 2

Upper curve: Reference water-curve for 1.9555 grams distilled water.
Lower curve: Observed volume change of 4.2836 grams toluene upon exposure to temperature change.

However, as later results will indicate, it became necessary to calculate the "water curve" one might expect with any given quantity of water. Also, it was desirable to correct the water curve shown in Fig. 2 in certain instances when relatively large quantities of solid materials were present in the system.

In order to make such calculations, it was assumed that the slope of the toluene-ice curve was determined almost entirely by the amount of toluene which was present. Therefore the quantity of toluene remaining in the dilatometer after the expansion produced by freezing would be directly related to the contraction which would result from lowering the temperature of the system. Fig. 2 shows the agreement which was found between the calculated water curve and the measured water curve, the calculated curve coinciding almost exactly with the experimental curve. Therefore, in later experiments a theoretical water curve was utilized, and in certain experiments corrections were made for the volume of the toluene displaced by the dry sample added to

the toluene-water system. Where these corrections were made, the value taken for the thermal expansion of toluene was that observed in these studies, rather than the theoretical coefficient of expansion of toluene.[25]

In Table II are given the readings from which the experimental water curve and the theoretical water curve were constructed.

TABLE I

Volume Change of Toluene with Temperature Change

Observed Temperature °C	Contraction of Capillary Toluene Column cm.
0.0	0.00
− 7.0	3.65
−19.0	10.50
−26.0	14.40
−31.0	17.25
−23.1	12.80
−12.1	6.60

TABLE II

The Volume Change of the System Toluene-water with Temperature Change
(1.9555 grams water, 4.2838 grams toluene)

Treatment and Process	Experimental Water Curve		Calculated Water Curve	
	Temperature °C	Length of Capillary Toluene Column cm.	Temperature °C	Theoretical Length of Capillary Toluene Column cm.
1st freezing	0.0	0.00	− 10.0	+18.40
	−11.1	+17.90	−20.0	+15.25
	−17.1	+16.10	−30.0	+12.20
	−23.0	+14.20	−40.0	+ 9.10
	−29.0	+12.35	−50.0	+ 6.00
	−31.0	+11.70		
	−34.1	+10.80		
	−40.6	+ 8.75		
	−48.0	+ 6.30		
	−43.7	+ 7.70		
	−39.9	+ 8.95		
	−37.5	+ 9.75		
	−32.0	+11.35		
	−18.0	+15.75		
	− 7.0	+19.25		
2nd freezing	0.0	0.00		
	−16.1	+16.30		
	−11.1	+17.85		
	− 5.0	+19.75		

As already noted, the density change which results when 1 gram of water freezes, causes an increase in volume of 0.090740 cc.[25] In the two determinations tabulated in Table II the expansion indicated a volume change of 0.094020 and 0.094025 cc. per gram of water. Again no cause can be assigned to this discrepancy. In no determination which we have made on the freezing of pure water was the theoretical value for expansion due to crystallization obtained. Accordingly, in the theoretical water curves constructed for our experiments we have taken our experimental value for the coefficient of expansion of water upon freezing.

Studies on gelatin.—The gelatin used in the following studies was Difco Standardized Bacto-gelatin. The product was not further purified. The samples were of air-dry granular gelatin taken from a tightly stoppered container. It was used air-dry, since oven-drying was found to produce a marked effect on the behavior of water-binding.

The dilatometer was filled as follows: The dry, granular sample of gelatin of the desired weight was first placed in the well-dried dilatometer bulb. The desired quantity of water was then pipetted into the dilatometer bulb and toluene was immediately added so as to preclude loss of water through evaporation. Toluene was added until the bulb was practically full, at which time the ground-glass stopper was tightly fitted into place and firmly secured. A very thin film of stop-cock lubricant was found to be of value in preventing leakage of the material in the dilatometer. By this method of filling, a small bubble of air would remain in the dilatometer, but the air was readily removed by passing a very fine wire through the capillary stem into the bulb. Then by holding the stem upright and exposing the dilatometer to small temperature fluctuations, the air was removed in a series of small bubbles. If the dilatometer contained an insufficient quantity of toluene, more was added by permitting the liquid to run down the fine wire into the capillary or bulb until the desired quantity was present.

The most serious obstacle encountered in these dilatometric studies was the appearance of an appreciable quantity of air during the process of freezing. This air was not held mechanically in the system nor was it held on the surfaces of small solid particles, for it could not be removed by reduced pressure and it appeared gradually, as a result of the freezing process. Distilled water, which had been boiled and cooled under toluene, readily "froze out" relatively large bubbles of air, which indicated that the air was held in solution. It was often necessary to repeat the freezing and thawing process from two to five times before records were taken in order to "freeze out" all of the air. The appearance of air, after freezing began, distorted the true shape of the curve, and therefore only those determinations in which no air appeared were accepted as indicating the behavior of colloidal systems upon freezing. Gelatin was found to give exactly reproducible data upon repeated freezings, which fact was accepted as evidence that the figures which are to follow represent a true picture of the freezing process.

In Fig. 3 and Table III are shown the data obtained by freezing 2.3080 grams of pure water in the dilatometer. The points when plotted with change in length of capillary toluene column as ordinates and with temperature as the axis of abscissae (as in Fig. 1), gave a straight line. When an approximately 10% gelatin gel containing the same weight of water was frozen in the same manner, an essentially straight line was again obtained. It will be noted that the readings taken during the warming of the frozen material fell, within experimental error, on the line drawn through the points given by the temperature-lowering process.
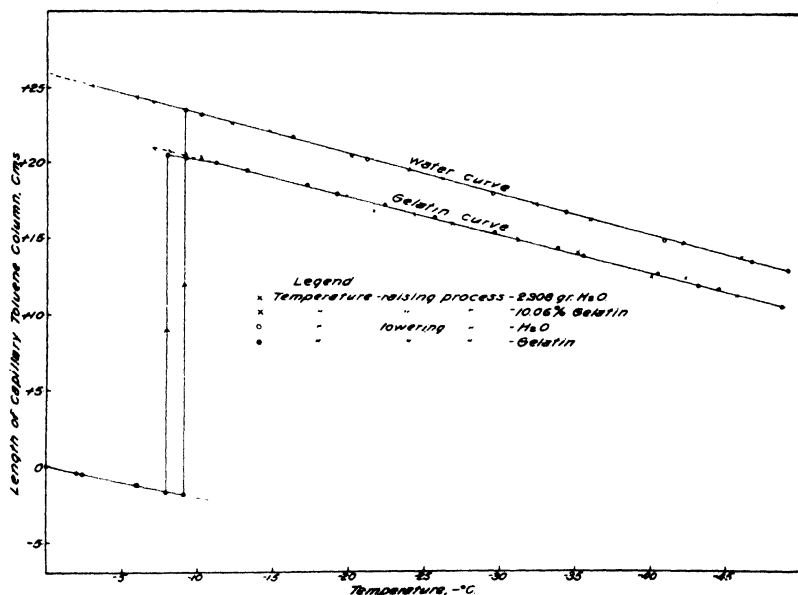
Fig. 3

The dilatometric behavior of a gelatin gel upon exposure to low temperatures.

Conclusions drawn by other workers [2,12,36,56] indicated that cooling the system gradually to lower and lower temperatures should cause a gradual and progressive freezing of the water in the system and that the resulting curve would resemble in general form the shape of vapor pressure curves obtained when similar materials are desiccated.

Fig. 3 shows that, almost within the limits of experimental error, the points of the temperature-raising curve fall on those of the temperature-lowering curve. Also that practically no change was found in the quantity of water which will freeze beyond the point at which initial freezing took place (-8.0°C) even though the temperature was dropped to -48.6°C.

Table IV and Fig. 4 show the effect of repeated freezing upon a gelatin gel. The gelatin curve is the result of two consecutive freezings, the first temperature lowering being to -48.6°C, the system then being raised to -6.0°C, and again lowered to approximately -60.0°C. Agreement between

TABLE III

Showing the Data obtained by freezing 2.3080 grams of Distilled Water and a 10.06% Gelatin Gel containing 2.3080 grams of Water

Distilled Water		Gelatin Gel	
Observed Temperature °C	Length of Capillary Toluene Column cm.	Observed Temperature °C	Length of Capillary Toluene Column cm.
0.0	0.0	0.0	0.0
− 2.4	− 0.5	− 2.0	− 0.45
− 6.0	− 1.2	− 6.0	− 1.30
− 9.1	− 1.8	− 7.9	− 1.70
− 9.1	+23.5	− 7.9	+20.50
−10.1	+23.2	− 9.1	+20.30
−16.1	+21.7	−11.1	+20.00
−21.0	+20.3	−13.1	+19.50
−29.3	+18.1	−17.1	+18.60
−34.2	+16.9	−19.0	+18.00
−41.7	+15.0	−22.2	+17.30
−46.6	+13.6	−25.5	+16.50
−49.0	+13.0	−29.5	+15.50
−45.9	+13.9	−33.7	+14.50
−40.7	+15.1	−35.4	+14.00
−35.8	+16.4	−40.3	+12.80
−26.0	+19.0	−43.0	+12.00
−20.0	+20.5	−44.4	+11.80
−14.1	+22.1	−48.6	+10.60
−12.1	+22.6	−45.6	+11.30
− 7.0	+24.0	−42.2	+12.60
− 3.0	+25.1	−40.7	+13.10
		−35.0	+14.20
		−29.2	+15.00
		−26.7	+16.10
		−21.5	+16.90
		−19.7	+17.90
		−11.1	+20.10
		−10.1	+20.40
		− 9.1	+20.60
		− 8.0	+20.80
		− 7.0	+20.90

the points representing each determination could hardly be closer, even though in the second case the temperature decrease was 20% greater than in the first. Particular attention is called to the fact that as shown by Fig. 4 the temperature-lowering and temperature-raising processes do not result in coincident lines. A consideration of this fact is not imperative at this time; rather, it is important that each line is the result of plotting the closely agreeing readings from two separate determinations.

In studying a system as concentrated as that reported in Table IV, it was found necessary in order to obtain a homogeneous gel to immerse the dilatometer in warm water and convert the mixture into a sol, which then was allowed to set to a gel. Accordingly, it was deemed advisable to ascertain whether or not the temperature at which peptization took place had any effect upon the subsequent freezing behavior of the system. Table V and Fig. 5
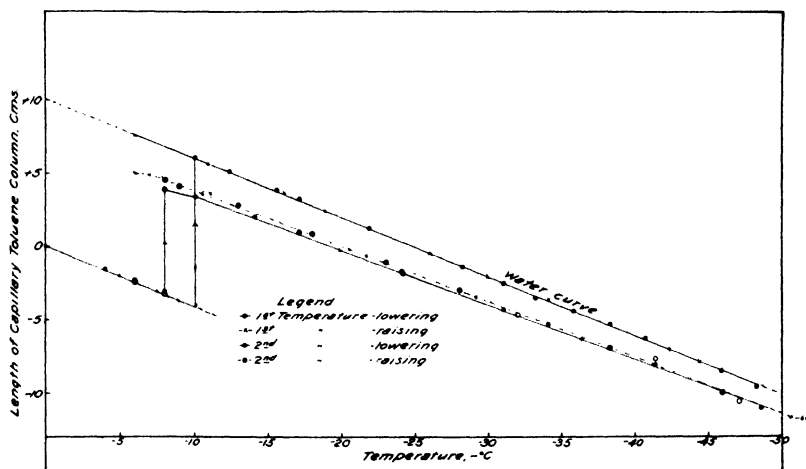
FIG. 4

The effect of repeated freezing upon the dilatometric behavior of a gelatin gel.
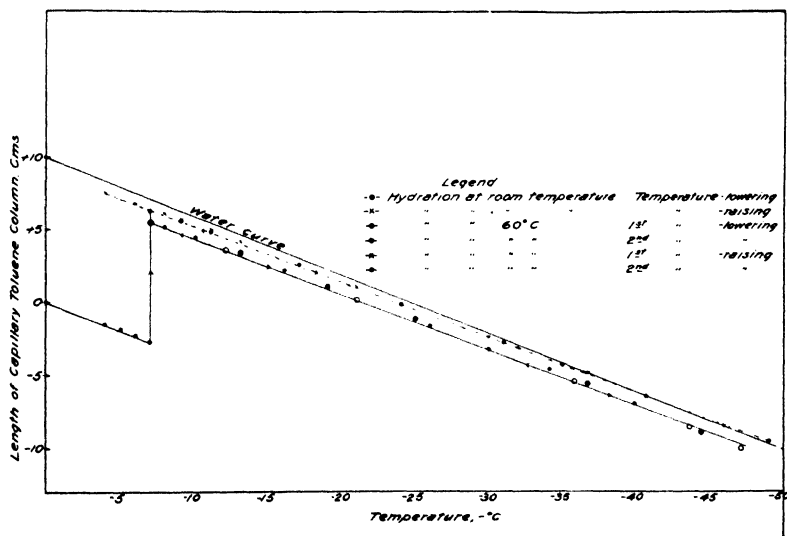
FIG. 5

The effect of the temperature of hydration upon the dilatometric behavior of a dilute gelatin gel upon exposure to low temperature.

TABLE IV

Showing the Data obtained by freezing 0.9300 gram of Distilled Water and a 50% Gelatin Gel containing 0.9300 gram of Water.

Distilled Water		Treatment and Process	0.4650 gm. gelatin + 0.9300 gm. H$_2$O	
Observed Temperature	Length of Capillary Toluene Column		Observed Temperature	Length of Capillary Toluene Column
°C	cm.		°C	cm.
0.0	0.00	1st freezing	0.0	0.00
− 5.0	−2.00		− 4.0	−1.55
− 7.5	−3.05		− 6.0	−2.25
− 8.2	−3.35		− 8.0	−3.05
− 9.0	−3.70		− 8.0	+3.85
−10.1	−4.00		−10.1	+3.40
−10.1	+6.00		−14.1	+2.00
−12.4	+5.05		−17.1	+1.00
−15.6	+3.85		−31.0	−4.25
−17.1	+3.25		−34.1	−5.35
−21.8	+1.25		−41.4	−8.05
−28.2	−1.40		−48.6	−11.05
−31.0	−2.50		−41.4	−8.10
−33.2	−3.40		−34.1	−5.25
−35.8	−4.40		−21.0	−0.20
−38.3	−5.30		−11.1	+3.60
−40.7	−6.30		− 9.1	+4.20
−45.9	−8.50		− 8.0	+4.55
−48.2	−9.65		− 7.0	+4.80
−44.4	−7.90		− 6.0	+4.95
−34.1	−3.60	Thawed and		
−26.0	−0.50	re-frozen		
−16.1	+3.65	2nd freezing	− 6.0	−2.45
− 6.0	+7.55		− 8.0	−3.20
			− 8.0	+3.85
			−17.1	+0.85
			−24.0	−1.70
			−32.0	−4.65
			−41.4	−7.65
			−47.1	−10.60
		*(approximated)	−60.0*	−14.25
			−45.9	−9.95
			−38.3	−6.85
			−28.0	−2.95
			−23.0	−1.05
			−18.0	+0.85
			−13.1	+2.70
			− 9.1	+4.05
			− 8.0	+4.65

show data resulting from such a study. In Fig. 5 the water curve for 0.9300 gram water from Fig. 4 has been drawn as a reference line. In this experiment 0.1000 grams of dry gelatin was added to 0.9300 grams of cold water, and the gelatin was allowed to swell for eight hours. The dotted line in Fig. 5 represents the curve obtained upon freezing the mixture. The gelatin curve gradually approaches the water curve, actually crossing it at the very low temperatures. This crossing may be explained by the fact that the water curve has not been corrected for the presence of the dry sample. It should be noted that there is no indication of gel alteration, since temperature-lowering and temperature-raising processes result in an identical line.
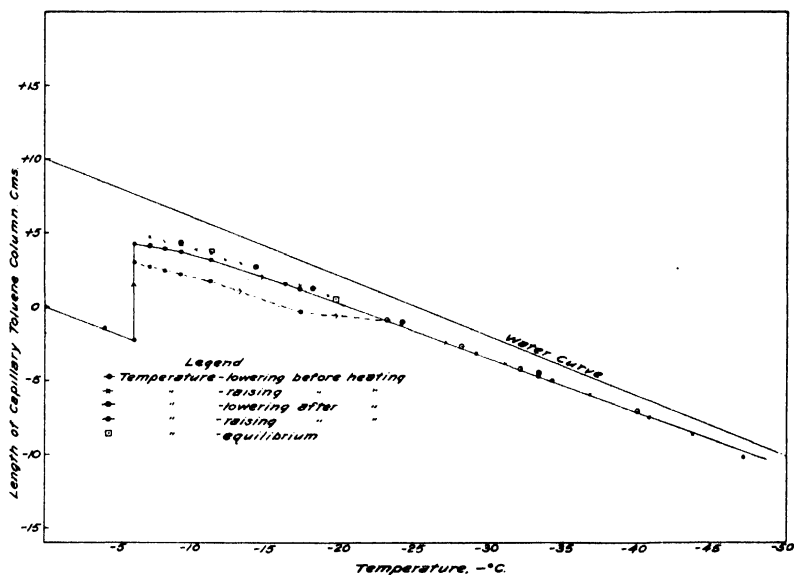
FIG. 6

The rate of establishment of equilibrium of ice formation in a 50% gelatin gel at different low temperatures with reference to the effect of elapsed time upon the subsequent behavior of the gelatin gel upon freezing.

The lower line of Fig. 5 is the plot of the data resulting from two consecutive freezings of the system described above after the hydrated gelatin has been converted to a sol by warming at a temperature of 60°C. Again, it is considered that no alteration was effected by freezing, as most of the readings from the two freezing processes lie on the same straight line.

It is evident from an inspection of the data in Table V and the graphs in Fig. 5 that the temperature at which gelatin is peptized plays a rôle in determining the water-binding capacity of a gelatin-gel as measured by dilatometric methods. The difference in water binding probably is the result of a more complete hydration of the ultimate gelatin particles when peptized at the higher temperatures. One may picture the gelatin hydrated at room temperatures as consisting of particles enveloped by thick shells of adsorbed water, with many particles still retaining their individuality as completely as

TABLE V

Showing the Effect of the Temperature at which Gelatin is peptized upon the Quantity of Water which remains unfrozen in a System of 0.1000 gm. Gelatin + 0.9300 gm. H_2O

Treatment and Process	Observed Temperature °C	Length of Capillary Toluene Column cm.	Treatment and Process	Observed Temperature °C	Length of Capillary Toluene Column cm.
Gelatin swelled 8 hours at room temperature, previous to freezing	0.0	0.00	Same sample warmed at approximately 60°C to form sol	0.0	0.00
	− 5.0	−1.85		− 4.0	−1.50
	− 6.0	−2.25		− 6.0	−2.25
	− 7.0	−2.70		− 7.0	−2.65
	− 7.0	+6.35		− 7.0	+5.55
1st freezing	− 9.1	+5.65		− 8.0	+5.20
	−11.1	+4.90		−10.1	+4.50
	−17.1	+2.65		−16.1	+2.25
	−24.0	−0.10		−26.0	−1.60
	−31.0	−2.70		−30.0	−3.20
	−35.0	−4.25		−34.1	−4.55
	−40.7	−6.45		−39.9	−6.95
	−48.0	−9.55			
	−60.0 (approx.)	−14.85			
	−45.9	−8.50	Same sample warmed to −1°C	− 7.0	+ 5.55
	−36.7	−4.80		−12.1	+ 3.65
	−30.0	−2.35	Re-frozen	−21.0	+ 0.25
	−21.0	+1.15	2nd freezing	−35.8	− 5.40
	−13.1	+4.20		−43.6	− 8.55
	−11.1	+4.95		−47.1	−10.05
	− 9.1	+5.70		−44.4	− 8.90
	− 8.0	+6.15		−36.7	− 5.55
	− 6.0	+6.85		−25.0	− 1.10
	− 4.0	+7.55		−19.0	+ 1.15
				−13.1	+ 3.45

Table VI presents data from a study of the effect of aging upon the behavior of a gelatin gel when frozen and also a study of the length of time which is required to establish an equilibrium in the freezing process. A part of the data in Table VI is graphed in Fig. 6.

The system was set up by adding 0.4650 grams of dry gelatin to 0.9300 grams of water and permitting it to swell at room temperature for three or four hours. The first freezing study is represented in Fig. 6 by the black dots (temperature-lowering) and by crosses (temperature-raising). A second freezing study was made after this system had stood at room temperature for 15 hours. The results of the second freezing are not plotted on the graph, but all points fell on the previously determined line. The system was then permitted to stand for five days at room temperature and when re-frozen at −11.1°C gave the same dilatometer reading as was obtained at this temperature for the first freezing. The system was now warmed in a water bath to 50°C for 20 minutes, resulting in the formation of a very viscous sol which upon cooling set to a gel. After standing at room temperature for 25 hours the system was again frozen. The temperature-lowering readings are represented in Fig 6 by the black circles and the temperature-raising curve by a cross within a circle.

It will be seen that equilibrium was apparently established at a much lower value of indicated free-water at temperatures from −6°C to −23°C than in the previous determinations. At temperatures lower than −23°C the readings all fell on the previously observed line. The temperature-raising curve coincides with the values previously obtained for the temperature-raising process.

In this instance an apparently decided effect was produced by the initiation of the crystallization process, as the readings between −6°C and −23°C differ so greatly in the temperature-lowering and temperature-raising processes.

With more dilute gelatin gels, Figs. 3 and 5, the temperature-raising and temperature-lowering curves coincided. Therefore it was assumed that some factor accompanying the increased concentration of the gelatin must be responsible for the lack of coincidence of the two curves in Fig. 6.

A pronounced retardation of the velocity of ice crystal formation resulted when any system in which material was dispersed in water was frozen. It was also apparent that the greater the concentration of the dispersed material, the greater was this retardation effect. This retardation of velocity of ice crystal formation has been observed with molecularly dispersed substances by Walton and Brann.[61] The velocity changes observed in our study have been similar to those reported by Callow[7] in a detailed study of the rate of ice crystal growth in super-cooled gelatin gels. Therefore it seemed probable that as the point of equilibrium was approached, crystal formation proceeded at such a slow rate that the small changes were not measurable in the time which we selected for observation.

In order to test this point, the system previously studied was thawed and re-frozen by holding it for a period of two hours at −18°C. The reading indicated that equilibrium had been established, as was shown by comparison

TABLE VI

A Study of the Effect of Time, Temperature and Repeated Freezings upon the Behavior of a 50% Gelatin Gel and upon the Establishment of Equilibrium in a Gelatin System—using Dilatometric Technic. Gelatin 0.4650 gram, Water 0.9300 gram

Treatment and Process	Observed Temperature	Length of Capillary Toluene Column
First freezing	0.0	0.00
Gelatin swollen at room temperature	− 4.0	−1.45
3-4 hrs.	− 6.0	−2.25
	− 6.0	+4.25
	− 7.0	+4.10
	− 8.0	+3.90
	− 9.1	+3.70
	−11.1	+3.15
	−16.1	+1.55
	−24.0	−1.25
	−34.1	−4.95
	−29.0	−3.15
	−40.7	−7.45
	−47.1	−10.15
	−43.6	−8.65
	−36.7	−5.95
	−31.0	−3.85
	−19.0	+0.75
	−13.1	+2.95
	−11.1	+3.60
	− 9.1	+4.20
	− 7.0	+4.70
Above sample thawed and kept at	0.0	0.00
room temperature for 15 hours	− 6.0	−2.30
Re-frozen	− 7.0	−2.65
2nd freezing	− 7.0	+4.15
	− 9.1	+3.70
	−11.1	+3.20
	−17.1	+1.20
	−33.2	−4.70
	−24.0	−1.25
	−17.1	+1.45
	−12.1	+3.20
	−10.1	+3.85
	− 8.0	+4.40

TABLE VI (Continued)

A Study of the Effect of Time, Temperature and Repeated Freezings upon the Behavior of a 50% Gelatin Gel and upon the Establishment of Equilibrium in a Gelatin System—using Dilatometric Technic. Gelatin 0.4650 gram, Water 0.9300 gram

Treatment and Process	Observed Temperature	Length of Capillary Toluene Column
Above sample thawed and kept at	0.0	0.00
room temperature for 5 days	−11.1	+3.15
3rd freezing		
Above sample thawed and held at	0.0	0.00
50.0°C for 20 minutes	− 5.0	−1.90
Stood at room temperature for	− 6.0	−2.20
25 hours	− 6.0	+3.00
Re-frozen	− 7.0	+2.70
4th freezing	− 8.0	+2.45
	− 9.1	+2.20
	−11.1	+1.70
	−17.1	−0.35
	−23.0	−0.90
	−28.0	−2.70
	−32.0	−4.20
	−39.9	−7.05
	−33.2	−4.45
	−24.0	−1.05
	−18.0	+1.25
	−14.1	+2.70
	− 9.1	+4.25
Sample from 4th freezing thawed	0.0	0.00
and re-frozen	− 7.0	−2.60
5th freezing	− 8.0	−3.00
	− 8.0	+2.55
	−11.1	+1.90
	−15.2	+1.20
	−18.0	+0.20
	−21.0	−0.80
	−23.0	−1.45
	−27.0	−2.85
	−31.0	−4.35
	−31.0	−4.25
	−41.4	−8.20
	−35.8	−6.00
	−26.0	−2.30
	−16.1	+1.60
	−10.1	+3.65

TABLE VI (Continued)

A Study of the Effect of Time, Temperature and Repeated Freezings upon the Behavior of a 50% Gelatin Gel and upon the Establishment of Equilibrium in a Gelatin System—using Dilatometric Technic.   Gelatin 0.4650 gram, Water 0.9300 gram

Treatment and Process	Observed Temperature	Length of Capillary Toluene Column
Above sample thawed at room temperature and re-frozen	−19.0	−0.60
6th freezing		
Held at −15.0° to −18.0°C overnight		
Above sample melted at 50.0°C and re-frozen. Held 2 hours at −18°C	0.0	0.00
	−19.5	−0.50
7th freezing	−15.2	−2.25
	−12.1	−3.30
	− 9.1	−4.05
Above sample melted at room temperature	−21.0	−0.10
	−16.1	+1.85
Frozen and held 1 hour at −21°C	−11.1	+3.50
8th freezing	− 9.1	+4.05
Above sample held at room temperature overnight		
To test time factor for equilibrium		
9th freezing		
Frozen and held at −11°C for:		
1.5 hours	−11.1	not in equilibrium
3.25 ”	−11.1	+2.35
5.25 ”	−11.1	+2.60
15.50 ”	−11.1	+2.60
Above sample cooled gradually from −11.0°C to −18.0°C over period of 7 hours	−20.0	0.00
	−15.2	+1.90
	−11.1	+3.30
Held at −19.0°C 13 hours	− 9.1	+3.95
10th freezing		

before they were hydrated, whereas if the somewhat hydrated mixture of gelatin and water is warmed to the point at which a sol is formed and is then permitted to cool, a jelly results which from all visible appearance is homogeneous. Presumably the particles in this gel present a greater area of interface to the water phase than does the system where only swelling has taken place.

with the previously determined values for $-19.5°C$, after the system had been subjected to a temperature as low as $-40°C$. In a repetition of the thawing and freezing process a period of 1 hour at $-21°C$ was found to give an equilibrium reading. However, on re-thawing and re-freezing at a temperature of $-11.1°C$, equilibrium was established only after a lapse of more than three hours.

These data are taken as evidence that the great difference observed between the temperature-lowering and -raising processes in the particular case represented in Fig. 6 (Table VI—4th and 5th freezings) is partially the result of lack of attainment of equilibrium in the crystallization process.

This may further explain the almost horizontal shape of the temperature-lowering curve (black dots) between the temperatures $-6°C$ and $-11°C$ in Fig. 6 and the similar flattening of the temperature-lowering curve of Fig. 4 between the temperatures $-8.0°C$ to $-10.00°C$. It is probably also the reason why in both Figs. 4 and 6 the temperature-raising curve lies slightly above the temperature-lowering curve. This difference in both cases is more marked at the temperatures nearer $0°C$, which is the temperature range at which establishment of equilibrium would be slower.

Undoubtedly another factor affects the behaviour of gelatin gels upon freezing. This is indicated by the dotted line in Fig. 6, but has been observed in other experiments.

In all of our dilatometer studies we have observed that the sols, gels, or even pure water would readily undercool to a temperature of from $-6.0°C$ to $-9.0°C$ before crystallization of ice began. It is possible that the size of the dilatometer and the relatively immobile condition in which the liquid was held was responsible for this great under-cooling. In one experiment, when the dilatometer was being standardized with a given quantity of distilled water, the water sample was broken into two nearly equal-sized globules, well separated from each other by a layer of toluene. Upon freezing, one globule froze at $-8.0°C$ and the system was held at this temperature until equilibrium was established. This equilibrium represented the freezing of only one globule of water. The temperature was then slowly lowered to $-11.0°C$, the contraction in the system continuing at a uniform rate. The second globule of water froze sharply at $-11.0°C$. In this instance, the only factor involved in the establishment of a second equilibrium was the second initiation of ice crystallization. Obviously the earlier apparent equilibrium between -8.0 and $-11.0°C$ was spurious.

The same effect is evident in the freezing of the gelatin gel represented by the dotted line in Fig. 6. Freezing began at $-6.0°C$. It progressed to a point at which about 50% of the water was frozen. Then for some unknown reason crystallization ceased and contraction set in with decreasing temperature. This contraction continued at a rate which indicated that no additional quantity of water was being frozen. At $-17.0°C$ crystallization began again and a true equilibrium was established at $-23.0°C$. This fact was even more evident to the experimenter than is indicated by the graph.

In order that this interrupted freezing may occur, it is not necessary to have an actual division of the sample, providing the portions are separated by some non-freezing substance. With the gelatin sample involved, the system had been warmed and mixed until it was apparently uniform. The gelatin gel, resulting from cooling, formed a continuous layer across the bottom of the dilatometer. Hardy,[21] in microscopical studies of freezing in gelatin gels, observed that the freezing process was intermittent in certain of his gels. He found that "when a pause occurs freezing starts again, not at the original face but at a new face within the gel, thus leaving the characteristic membrane of dehydrated gel behind."
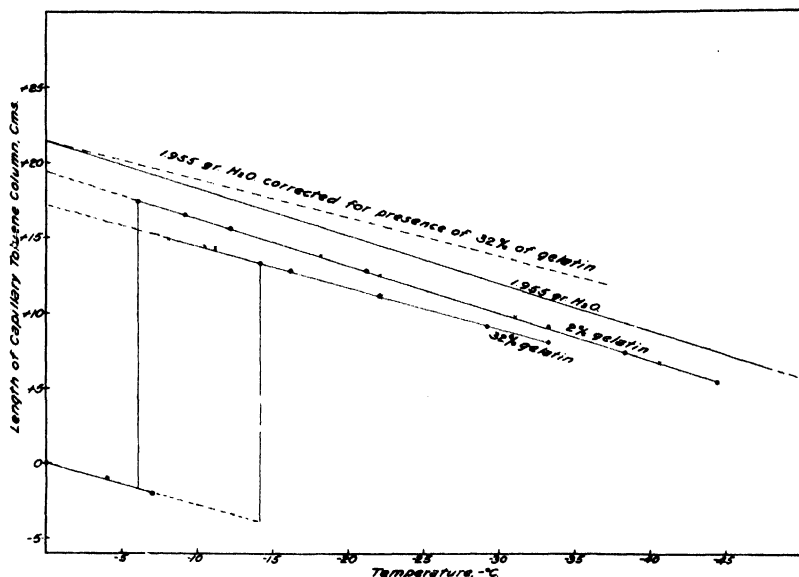
FIG. 7

The effect of concentration upon the dilatometric behavior of gelatin gel upon exposure to low temperatures.

The "intermittent freezing process" postulated by Hardy and the observed interrupted freezing noted above may be due to different causes. However, the evidence presented by Hardy demonstrates the formation of an actual boundary between a freezing portion and yet unfrozen portions of the same sample. Hardy also pointed out that in certain phases of intermittent freezing the process occurs "too slowly to be followed." Thus it may be that the intermittent process proceeds at an irregular or interrupted rate.

The significance of an interrupted freezing process in elastic gels cannot be overlooked when one is studying frozen samples by physico-chemical technic. It must also be considered in determining the temperature at which a sample should be frozen.

Fig. 6 shows that maximum freezing occurs at a temperature not lower than $-11.1°C$ if sufficient time (5 hrs.) is given for the establishment of

equilibrium. Equilibrium is attained at $-21.0°C$ in less than 1 hour, but there is no evidence that more water crystallized at $-21.0°C$ than at $-11.1°C$, once equilibrium is attained.

A few experiments were made involving the behavior of gelatin gels of varying concentrations during the process of freezing. The data are presented in Table VII. Fig. 7 is a graphical presentation of the data obtained from the most dilute concentration (2%) and the highest concentration (32%).
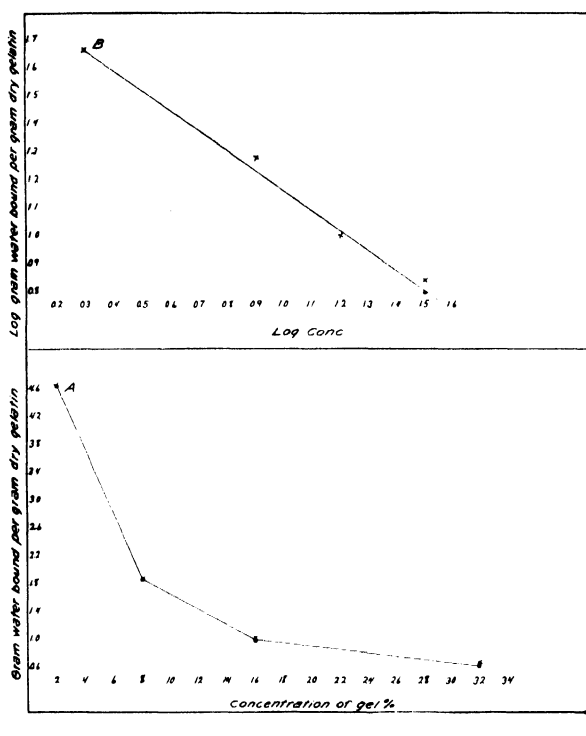
FIG. 8

Showing the weight of water bound in gelatin gels of different concentrations at the temperatures of $-10.0°C$ and $-30.0°C$. Expressed as gram water bound per gram dry gelatin.

In these studies 1.955 grams of water and the desired weight of gelatin were mixed and warmed to the point at which solation was complete. With the 2% sol no correction was made for the effect of dry gelatin in the system. It will be seen that at $-6.0°C$, the point of initial freezing, the indicated bound-water content is 9.35%. At a temperature of $-44.4°C$, the bound-water content is, within experimental error of the method, exactly the same (9.35%). It is also shown that one is justified in considering the temperature-lowering and temperature-raising curve as a straight line.

The same may be said of the curve representing the freezing of the 32% gel. The behavior was observed between the temperatures of $-8.0°C$ and $-32.0°C$, and all points fall easily on a straight line. If now the observed

TABLE VII

Data showing the Effect of Freezing upon Gelatin Gels of Different Concentrations— using Dilatometric Technic

2% gelatin gel		16% gelatin gel	
.0391 grms. gelatin 1.955 grms. water		.3128 grms. gelatin 1.955 grms. water	
Observed Temperature °C	Length of Capillary Toluene Column cm.	Observed Temperature °C	Length of Capillary Toluene Column cm.
0.0	0.00	0.0	0.00
− 4.0	− 1.00	−11.1	+14.70
− 6.0	+17.40	−25.0	+10.70
− 9.1	+16.55	−32.0	+ 8.70
−12.1	+15.60	−39.9	+ 6.50
−21.1	+12.80	−47.2	+ 4.30
−33.2	+ 9.10	−38.3	+ 6.90
−38.3	+ 7.40	−24.0	+11.00
−44.4	+ 5.40	−16.1	+13.35
−40.6	+ 6.75	− 9.1	+15.35
−31.0	+ 9.75		
−22.0	+12.50		
−18.1	+13.80		
− 9.1	+16.60		

8% gelatin gel		32% gelatin gel	
0.1564 grms. gelatin 1.955 grms. water		0.6256 grms. gelatin 1.955 grms. water	
Observed Temperature °C	Length of Capillary Toluene Column cm.	Observed Temperature °C	Length of Capillary Toluene Column cm.
0.0	0.00	0.0	0.00
− 4.0	− 1.10	−14.1	+13.35
− 7.0	+16.10	−16.1	+12.85
− 9.1	+15.55	−22.0	+11.20
−11.1	+15.00	−29.1	+ 9.15
−13.1	+14.40	−33.2	+ 8.05
−21.0	+12.00	−22.0	+11.20
−33.2	+ 8.45	−11.1	+14.30
−39.9	+ 6.50	− 8.1	+14.90
−48.0	+ 3.90		
−36.7	+ 7.35		

Thawed and re-frozen

0.0	0.00
−17.1	+13.15
−13.1	+14.35
− 9.1	+15.55

water curve be corrected for the presence of the dry gelatin (as indicated in Fig. 7 by the dotted line), the percentage of bound-water present at −8.0°C is 20.56 and at −33.0°C is 22.43. This most concentrated gelatin gel curve, then, may be considered as practically a straight line parallel to the theoretical water curve. The expression of the percentage of bound-water at the temperatures − 10.0°C and − 30.0°C gives an indication of the degree of parallelism between the observed gelatin curve and the theoretical water curve. Table VIII shows an actual slight *decrease* in total free-water content when the temperature is lowered from − 10.0°C to −30.0°C. This is the reverse of what would be expected if bound water were converted into ice by a lowered temperature.

Corrections for volume of toluene displaced by the sample were based on the density of dry gelatin. Thus, knowing the weight of the dry gelatin used in the determination, the volume of toluene displaced by the gelatin could be calculated. The density of the gelatin was determined experimentally and was found to be 1.385. This method of correction is subject to question, for it is known that the volume occupied by gelatin after being wetted by water is actually less than the sum of the volume of the dry gelatin plus the volume of the water taken. Svedberg[57] found the contraction caused by wetting gelatin to be in the neighborhood of 0.055 cc. per gram of gelatin. This value is so low that this could not be the source of appreciable error under the conditions of our experiments. His study does justify the question, however, as to what may be the actual volume of the "frozen-out" gelatin.

Table VIII and Fig. 8 show the data for bound water in gelatin gels at − 10°C to − 30°C, as calculated from the dilatometer readings recorded in Table VII. The calculations have been expressed in the grams of water bound per gram of dry gelatin. Freundlich[16] has given a general expression for an adsorption reaction which expressed mathematically is the equation for a parabola. The logarithmic expression of a parabolic curve is a straight line.

Plotting the arithmetic values of Table VIII, where the abscissa represents the grams water bound per gram dry gelatin and the ordinate represents the concentration of the gelatin gel, a smooth curve (A-Fig. 8) was obtained which appeared to be parabolic. When the logarithmic values were plotted, the resulting points fell practically on a straight line (B-Fig. 8). Accordingly it appears probable that water-binding in gelatin systems is an adsorption reaction.

TABLE VIII
The Bound Water in Gelatin Gels as a Function of Gel Concentration

Gel Concentration	Bound water expressed as per cent of total water in system		Water bound per gram dry gelatin	
	−10°C	−30°C	−10°C	−30°C
%	%	%	grams	grams
2	9.35	9.35	4.675	4.675
8	15.10	15.19	1.888	1.899
16	16.16	16.82	1.010	1.051
32	20.56	22.43	0.643	0.701

All of the studies which we have made on gelatin gels were made on gels prepared from essentially iso-electric gelatin (pH 4.7–4.8). Some experiments were made to study the effect of varying pH upon the dilatometric behavior of dilute gelatin gels when exposed to low temperature, but no observable difference due to a pH effect could be detected.
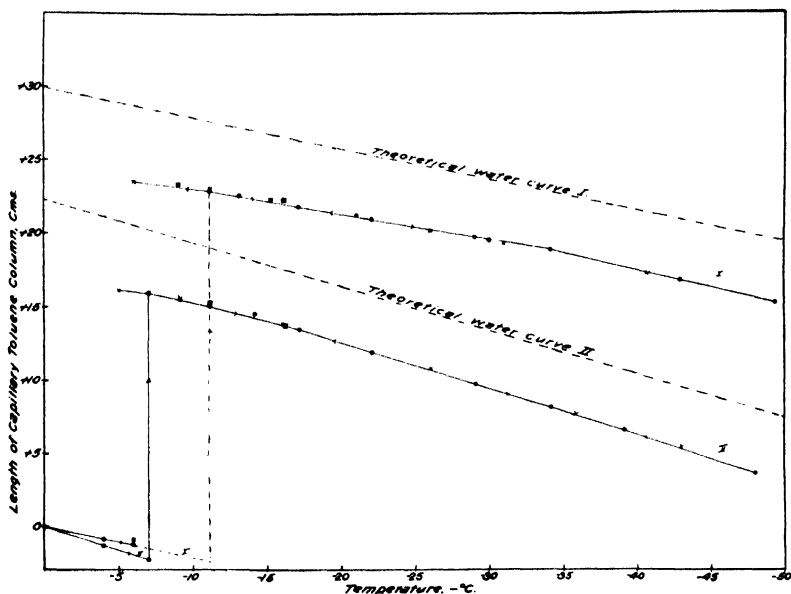
FIG. 9

The dilatometric behavior of the thick portion of egg white upon repeated exposure to low temperature.

The Behavior of the Thick Portion of Egg White from Fresh Eggs upon Freezing.—A short study was made upon the thick portion of the white of fresh eggs. This material was chosen as a natural hydrophilic colloidal system which would serve to extend the range of the bound-water studies. No attempt has been made to conduct a complete study of the behavior of egg white upon freezing.

Dilatometric analyses were made of two samples taken from two eggs not more than six hours old. The sample taken in each instance was a portion of the unmixed thick white of one egg. It was considered, as has been pointed out by St. John,[53] that mechanical mixing of the egg white would alter the colloidal nature of the system.

The experimental data obtained from this study are given in Table IX and Fig. 9.

These data indicate that in each sample the freezing process was completely reversible. The readings for the temperature-raising process when plotted fell on the curve representing the temperature-lowering process. Also, the data taken during a second freezing determination fell practically on the curve representing the first freezing process.

In this respect the behavior of egg white was similar to that previously observed for gelatin. However, with egg white the curves obtained were not straight lines. A more surprising fact was that they receded somewhat from the theoretical water curve at the lower temperatures. This is clearly indicated in Fig. 9 and shown numerically in Table X. The fact that the observed curve gradually receded from the theoretical curve was an indication of a contraction greater than would be expected from thermal contraction alone. If some of the "bound" water had frozen we should expect an expansion.

Egg white cannot be considered a chemical entity but is a colloidal system containing egg albumin and other proteins.

Table IX

A Dilatometric Analysis of the Effect of Freezing of the Thick White of Fresh Hen's Eggs

Sample 1

Weight 3.1929 grams. Water 85.68%

	Observed Temperature °C	Length of Capillary Toluene Column cm.
1st freezing	0.0	0.00
	− 4.0	− 0.85
	− 6.0	− 1.25
	− 9.1	—
	−11.1	+22.85
	−13.1	+22.55
	−17.1	+21.85
	−22.0	+21.00
	−30.0	+19.55
	−34.1	+18.90
	−43.0	+16.80
	−49.4	+15.25
	−40.7	+17.25
	−31.0	+19.30
	−16.1	+22.30
	− 6.0	+23.50
Thawed and re-frozen	− 6.0	− 0.90
2nd freezing	− 9.1	+23.20
	−11.1	+22.95
	−15.2	+22.30
	−21.0	+21.25
	−29.0	+19.70
	−34.1	+18.90
	−26.0	+20.20
	−16.1	+22.20

TABLE IX (continued)

A Dilatometric Analysis of the Effect of Freezing of the Thick White of Fresh Hen's Eggs

Sample 2

Weight 2.3008 grams. Water 88.53%

	Observed Temperature °C	Length of Capillary Toluene Column cm.
1st freezing	0.0	0.00
	− 4.0	− 1.30
	− 7.0	− 2.25
	− 7.0	+15.90
	− 9.1	+15.50
	−11.1	+15.05
	−14.1	+14.50
	−17.1	+13.45
	−22.0	+11.90
	−29.0	+ 9.75
	−34.1	+ 8.20
	−39.1	+ 6.65
	−48.0	+ 3.65
	−43.0	+ 5.40
	−35.8	+ 7.70
	−26.0	+10.80
	−16.1	+13.85
	− 9.1	+15.60
	− 6.0	+16.10
Thawed and re-frozen	−16.1	+13.85
2nd freezing	−11.1	+15.20

Sörensen[55] made an extended study of crystalline egg albumin. His crystals were separated under conditions of carefully controlled concentrations of hydrogen ions and ammonium sulfate. He found that the crystals were actually hydrous egg-albumin sulfate containing 0.22 grams water per gram dry albumin.

From the fact that egg albumin may be separated in the crystalline form from a colloidal system, it seems possible that the observed greater contraction of egg white at low temperature might be due to an orientation of the hydrated egg albumin into a definite crystal lattice. This crystallization resulting from exposure to the low temperatures would take place with the formation of a more closely packed space lattice and accordingly contraction would result.

Studies on Systems of the Non-elastic-Gel Type

Studies on Activated Silica Gel.—Pulverized silica gel, obtained from the Silica Gel Corporation, was sieved; the portion which passed through the 60-mesh and was held on the 80-mesh sieve was utilized in this study. This portion was activated by heating in a vacuum oven at 150°C for 2 hours.

Systems were set up by mixing 0.4888 gram, 1.1730 grams, and 1.574 grams of activated silica gel with 1.955 grams of distilled water. Heat was liberated when the silica gel was wetted, giving evidence of a decided adsorption of
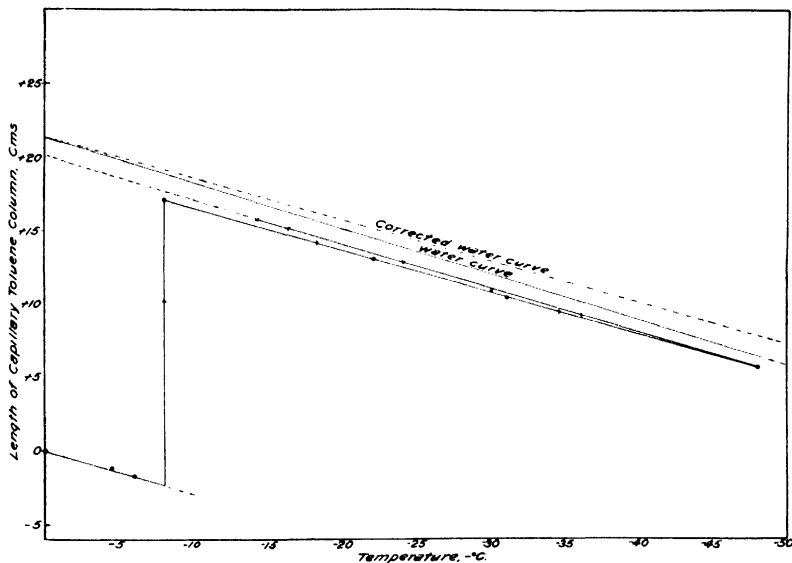
FIG. 10

The dilatometric behavior of the system Activated Silica Gel-Water upon exposure to low temperature. (System consisting of 1.955 grams distilled water and 0.4888 grams Activated Silica Gel).

water. Table XI shows the dilatometric records which were made on the 25%, 60% and 80.5% silica gel systems. The data are graphed in Figs. 10, 11 and 12. In these figures correction has been made for the volume occupied by the dry silica gel, taking 2.20 as the density.

Fig. 10 shows the shape of the curve and the general agreement of experimental data obtained when the 25% mixture was frozen to −48.0°C. The points of the temperature-lowering curve fall on a straight line which is practically parallel to the corrected water curve. The line marked with the black crosses represents the temperature-raising curve. These points also fall on a straight line, but as the temperature is raised this line slowly diverges from the temperature-lowering curve.

Fig. 11 is the graphical representation of the effect of freezing upon a 60% activated silica gel system. The black dots on line AB represent the readings taken during the first freezing. The line BC represents the slope of the tem-
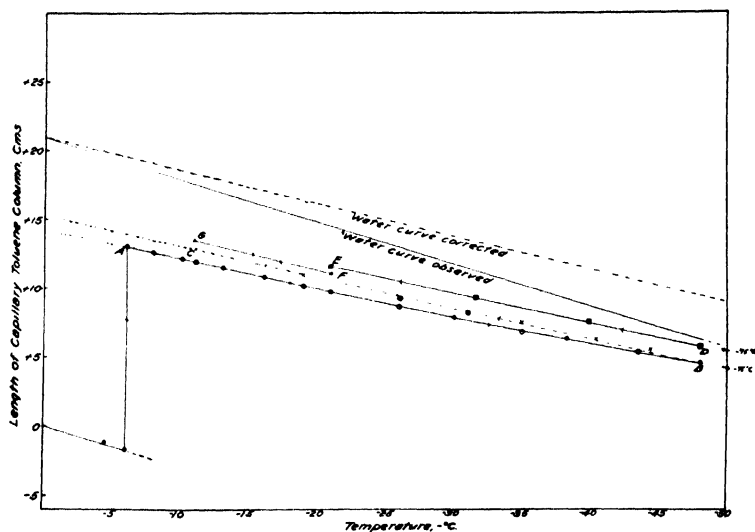
FIG. 11

The dilatometric behavior of the system Activated Silica Gel-Water upon repeated exposure to low temperature. (System consisting of 1.955 grams distilled water and 1.173 grams Activated Silica Gel).

TABLE X

A Dilatometric Study of the Thick White of Fresh Hen's Eggs. The Bound Water calculated from the Expansion which was observed due to Ice Formation and the Theoretical Expansion which should have resulted if the Total Water present had frozen

	"Apparent Bound-Water" at Different Temperatures Expressed as % of Total Water Present in System	
Temperature °C	Sample 1 %	Sample 2 %
− 6.0	17.36	20.18
−10.0	16.19	18.16
−20.0	14.86	17.26
−30.0	13.36	17.71
−40.0	13.36	18.16
−48.0	14.36	19.73

perature-raising curve. Again, this is a straight line lying decidedly above the temperature-lowering curve.

The sample was then thawed and a second freezing was conducted. The open circles, representing these readings fall on the previously formed line. The temperature was again raised to − 26.0°C and the two readings taken were found to fall on the corresponding line of the first temperature-raising process.

Fig. 12

The dilatometric behavior of the system Activated Silica Gel-Water upon repeated exposure to low temperatures. (System consisting of 1.955 grams distilled water and 1.574 grams Activated Silica Gel.)

Accordingly, repeated freezings gave reproducible data,* which indicated that no alteration of gel structure had resulted from the freezing process.

At this time the sample which was at a temperature of $-26.0°C$ was cooled to an approximated temperature of $-75°C$. Readings were then made as the temperature was raised to $-21.0°C$. Line DE represents the curve obtained. Point D lies very decidedly above point B, indicating that an appreciably greater quantity of water has been frozen at $-75.0°C$ than at $-48.0°C$. After warming the sample to $-21.0°C$ (point E) it was held at this temperature for 3 hours. A reading then taken has been represented by point F. Point G indicates the reading when the sample was warmed at $-11.0°C$. On again lowering the temperature to $-21.0°C$, without further thawing the system, it was found that the equilibrium had not been disturbed.

Fig. 12 represents the behavior of the 80.5% mixture upon being frozen. The first temperature lowering was to only $-33.2°C$. The black dots and black

*It should be added that this statement holds when the termination of the temperature-lowering process has been at approximately the same temperature. Thus practically no hysteresis could be observed between the first and second temperature-raising processes, the termination of the first and second temperature-lowering processes being $-48°C$ and $-43.6°C$ respectively. Hysteresis appeared when the system was cooled to varying low temperatures. There is a decided difference in bound water values (cf. Table XII) at the same temperatures of the temperature-raising process when the termination of the temperature-lowering process has been different. Consider as an example the first and third temperature lowering processes which terminated at $-48°C$ and $-75°C$ respectively. With the 80% Activated Silica Gel-Water system the termination of the first and second temperature-lowering processes were $-33.2°C$ and $-49.4°C$ respectively. Accordingly this system likewise showed the effect of the lowest temperature reached in the freezing process. The differences in the bound water values represented at the different temperatures in Table XII are, we believe, due to the conditions mentioned above.

TABLE XI

A Dilatometric Study of the Effect of Freezing upon Systems of Activated Silica Gel and Water

	System I			System II			System III	
	Activated Silica Gel 0.4888 gram	water 1.9550 grams		Activated Silica Gel 1.1730 grams	water 1.9550 grams		Activated Silica Gel 1.5740 grams	water 1.9550 grams
Treatment and Process	Observed Temperature	Length of Capillary Toluene Column	Treatment and Process	Observed Temperature	Length of Capillary Toluene Column	Treatment and Process	Observed Temperature	Length of Capillary Toluene Column
	°C	cm.		°C	cm.		°C	cm.
1st freezing	0.0	0.00	1st freezing	0.0	0.00	1st freezing	0.0	0.00
	− 8.0	+17.05		− 6.0	+13.00		− 9.1	+11.15
	−22.0	+13.05		− 8.0	+12.55		−11.1	+10.75
	−31.0	+10.40		−10.1	+12.10		−16.1	+ 9.75
	−48.0	+ 5.65		−13.1	+11.45		−27.0	+ 7.65
	−30.0	+10.95		−16.1	+10.80		−33.2	+ 6.65
	−24.0	+12.80		−21.0	+ 9.70		−21.0	+ 9.00
	−14.10	+15.75		−30.0	+ 7.90		−13.1	+10.70
				−38.3	+ 6.35		− 7.0	+12.10
				−43.6	+ 5.55		− 6.0	+12.35
				−48.0	+ 4.65	Held at −20°C		
				−44.4	+ 5.60	for 2.5 hrs.	−22.0	+ 8.55
				−41.4	+ 6.30		−11.1	+10.95
				−35.0	+ 7.55		− 6.0	+12.10
				−26.0	+ 9.25	Thawed and		
				−19.0	+10.90	refrozen	−11.1	+10.70
				−11.1	+12.80	2nd freezing	−21.0	+ 8.70
							−30.0	+ 7.10

TABLE XI (Continued)

A Dilatometric Study of the Effect of Freezing upon Systems of Activated Silica Gel and Water

System II			System III		
Activated Silica Gel 1.1730 grams		water 1.9550 grams	Activated Silica Gel 1.5740 grams		water 1.9550 grams
Treatment and Process	Observed Temperature	Length of Capillary Toluene Column	Treatment and Process	Observed Temperature	Length of Capillary Toluene Column
	°C	cm.		°C	cm.
Thawed and refrozen				−34.1	+ 6.50
2nd freezing	−11.1	+11.85		−45.9	+ 5.05
	−19.0	+10.10		−49.4	+ 4.45
	−26.0	+ 8.65		−41.4	+ 6.40
	−35.0	+ 6.85		−35.8	+ 7.45
	−43.6	+ 5.40		−21.0	+10.15
	−31.0	+ 8.20		−11.1	+12.45
	−26.0	+ 9.25		− 7.0	+12.90
	−75.0	—			
	−48.0	+ 5.80			
	−39.9	+ 7.60			
	−31.0	+ 9.30			
	−21.0	+11.50			
Held 3 hours at −21.0°C	−21.0	+11.05			
	−11.1	+13.45			
	−21.0	+11.05			
	−11.1	+13.45			

crosses represent the readings taken during the temperature-lowering and temperature-raising processes, respectively. A second temperature lowering was made to 49.5°C. The readings of the second process lie on the previously obtained straight line to the temperature of −30.0°C. At this point, as in Fig. 11, the curve makes a decided convergence toward the water curve. The temperature-raising process from the temperature −49.5°C gives a line lying considerably above that given when the sample was frozen to only −33.2°C.

In Figs. 10, 11 and 12 the observed water curve for 1.9550 grams of water has been drawn. The water curve corrected for the volume of silica gel has been represented by a dotted line. Table XII shows the percentage of bound-water found at different temperatures, the corrected water curve being in all cases considered to represent 100% of free water.

The behavior of the activated-silica gel-water systems is very different from that of the system, gelatin-water. These differences are (A) the temperature at which maximum freezing occurred and (B) the behavior of the

frozen mass as the temperature approached the melting point of ice. In the gelatin systems maximum freezing was complete at temperatures not lower than −6.0°C and further cooling of the frozen mass to −48.0°C was without apparent effect on the bound water content of the gelatin.

With the silica gel systems gradually lowering temperatures caused increasing quantities of water to freeze; also, the temperature-raising curve lay distinctly above that for the temperature-lowering process.

TABLE XII

Showing the Apparent Per Cent of Total Water existing as Bound Water in Systems of Activated Silica Gel-Water at Different Low Temperatures

Concentration of system per cent	Process	Bound Water at Temperature Indicated				
		−10°C per cent	−20°C per cent	−30°C per cent	−40°C per cent	−48°C per cent
25	Temp. lowering	9.35	9.81	9.90	10.02	10.28
25	Temp. raising	8.01	7.94	8.64	9.30	10.28
60	Temp. lowering	29.90	28.50	27.57	25.47	22.90
60	Temp. raising, 1st	25.70	25.00	24.30	23.83	22.90
60	Temp. raising, 3d*	—	—	19.16	18.23	17.52
80	Temp. lowering	38.32	37.15	35.28	31.07	27.58
80	Temp. raising, 1st	35.75	35.75	35.28	—	—
80	Temp. raising, 2nd	31.54	30.14	28.97	27.80	26.87

* Second temperature raising not calculated.

If the behavior of inelastic gels upon freezing is analogous to that of elastic gels as indicated by gelatin, the curves representing the temperature-lowering and raising processes should be the same, and decreasing temperatures would not increase the amount of water that could be frozen.

Again, if silica gel consists of a mass possessing a structure extremely capillary in nature, as is conventionally accepted,[10,34,46,47] it can be seen that the water in the gel must be held with a very great force of capillarity. This force is sufficiently great to resist the forces of crystallization when the temperature is lowered below the freezing point of water, keeping the water adsorbed in a liquid state. Finally, as the temperature is lowered the crystallization force becomes great enough to cause the capillary water to freeze. If the temperature be now raised a slight amount, it would seem that equilibrium should be established anew between the opposing forces of capillarity and crystal formation, with the result that some of the frozen water would melt and again become adsorbed capillary water. This would result in a completely reversible process, with the temperature-lowering and temperature-raising curves following the same path in spite of the fact that decreasing temperatures caused an increase in the quantity of water which could be frozen. That the freezing of silica gel systems is not a readily reversible process is indicated by Figs. 10, 11 and 12.

However, Figs. 11 and 12 and Table XII indicate that a partially reversible reaction takes place in the 60% and 80.5% samples. The slope of the temperature-raising curves in Figs. 11 and 12 is divergent from the corrected water curve, indicating that actually less free-water is present at −10.0°C after the sample has been warmed from −48.0°C than is present at the point of −48.0°C. The same tendency is more clearly indicated in Fig. 11 by the points E and F. E was the reading given when the frozen mass which had
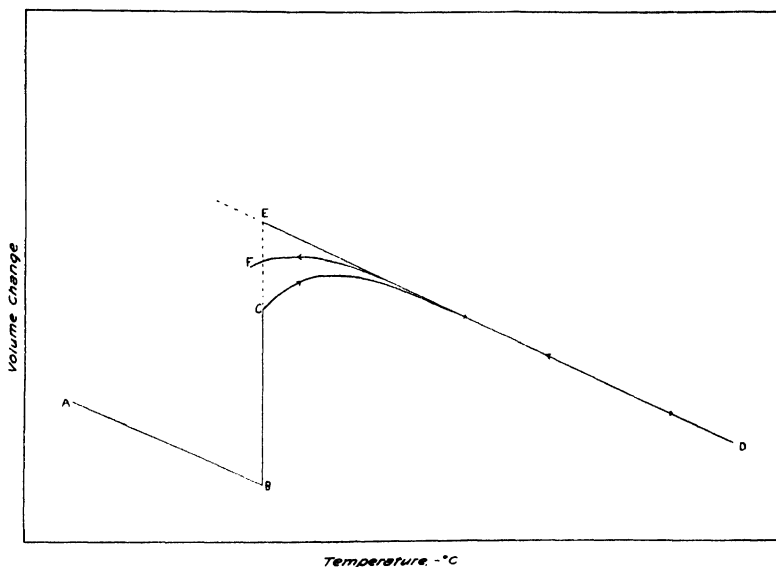
FIG. 13

The general dilatometric behavior of inorganic hydrogels upon exposure to low temperature, as observed by Foote and Saxton.

been cooled to −75.0°C was slowly and gradually warmed to −21.0°C. When the temperature was held at −21.0°C for several hours, point F was found to be the measured value for that temperature, rather than E. Evidence that this is nearer the true point of equilibrium is shown by the facts that (a) after raising the temperature to −11.0°C the same value was obtained when the temperature was again lowered to −21.0°C and (B) when the lines DE and FG are extended they are found to intersect at the 0.0°C line.

This difference between the points E and F would indicate that the velocity of equilibrium establishment is a factor determining in some degree the slope of the temperature-raising curve. Time cannot be considered the only factor, for after a period of three hours the line FG, which apparently represents the points of true equilibrium, lay distinctly above the corresponding portion of the line BC. Evidently, then, some difference was produced in the point of true equilibrium when the sample was cooled to −75.0°C rather than only to −48.0°C.

Studies on Colloidal Ferric Hydroxide Systems.—We have already noted that Foote and Saxton[13,14,15] investigated the effect of freezing upon certain

inorganic colloidal systems. The general shape of the Foote and Saxton curve is indicated in Fig. 13. They assumed that three kinds of water existed in their gels, (A) "free-water," (B) "apparent capillary-water," (C) "combined-water." The free-water was considered to be the water which froze readily at a constant temperature. This is indicated in Fig. 13 by the vertical line BC. As the temperature was gradually lowered to point D, the curved line CD was obtained. The gradual freezing, represented by the curved line, was considered a freezing of water held in the capillary spaces of the gel. Raising the temperature from D to near the zero point gave the line DF. DE is a straight line formed by an extension of the straight portion of line DF. DE was considered the theoretical measure of the combined water. The gradual sloping away of DF from DE was considered to be due to the remelting, as the temperature approached 0.0°C, of some of the water held by capillarity. As Foote and Saxton were unable to find a point at which there appeared to be a sharp distinction between "free-water" and "apparent capillary-water" they empirically chose −6.0°C as the temperature at which all "free-water" was frozen. The vertical distance between the observed point C and the extrapolated point E was considered to be a measure of the "apparent capillary-water."

Our results are at variance with those of Foote and Saxton. We have shown that with gelatin, if sufficient time were given for equilibrium to be established at the point of initial freezing, the line CD was a straight line and the line DF was also a straight line coinciding with CD. With activated silica gel, lines CD and DF were both straight, though not coincident.

It seemed that two possible explanations might be advanced for the curved line obtained by Foote and Saxton, (A) that a true equilibrium was not established at the temperature of initial freezing (their point C) before the temperature was again lowered, or (B) that the sample, if not electrolyte-free, would at first freeze gradually and also begin to melt at temperatures lower than zero.

The following experiments were carried out on a hydrated ferric hydroxide coagulum to clarify, if possible, the points in question. The hydrated ferric hydroxide-gel was prepared as follows: 100 cc. of 30% ferric chloride solution was added to 400 cc. of boiling water. The colloidal ferric hydroxide which formed was precipitated by the addition of a sufficient amount of dilute ammonium hydroxide. The coagulum was dialyzed against distilled water until no chlorides appeared in the external liquid. The coagulum was filtered and sucked as dry as possible upon a Büchner funnel. The mass of ferric hydroxide was then well mixed and aged for several days over distilled water in a closed vessel. The resulting ferric hydroxide, although having a moisture content of from 85-88%, had the consistency and appearance of thick apple butter. Tables XIII and XIV and Fig. 14 show the data resulting from the dilatometric measurements made upon this hydrated ferric hydroxide.

System I consisted of a 3.541 gram sample containing 84.22% water. Initial freezing took place at −6.0°C, and after freezing was complete the contraction-expansion curve to −48.0°C was a straight line. As the temperature was gradually raised to −6.0°C there resulted a second straight

line, but as in the activated silica gel studies, the temperature-lowering and temperature-raising curves were divergent from the point of lowest temperature.

Determination II is a repetition of determination I. In System II the sample weighed 2.7071 grams containing 85.25% water. The solid black lines of this part of Fig. 14 represents the results of the first freezing process. In this determination, as in the former, the points of the temperature-lowering and temperature-raising process lie on straight lines diverging from the point of lowest temperature.
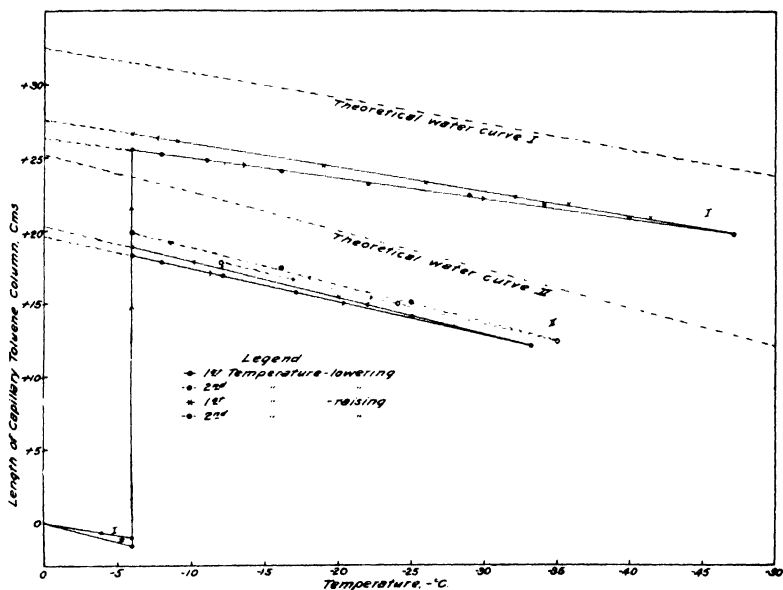
FIG. 14

The dilatometric behavior of hydrous ferric hydroxide upon exposure to low temperature.

With both samples I and II freezing was observed to result in a very decided physical alteration. When the sample was thawed, the ferric hydroxide settled in brown flakes from clear water, the water representing a large percentage of the total volume of the sample. Thus the "apple butter" consistency of the coagulum was completely disrupted. Accordingly a second freezing was made of sample II. Readings of this freezing are indicated by open circles and by a cross within a circle. The resulting lines follow closely the lines of the first freezing process.

In this study with ferric hydroxide the results coincide in many respects with those found by Foote and Saxton, with the exception that all of these readings fell on straight lines, while those of Foote and Saxton curve decidedly between the temperature $-10.0°C$ and $-6.0°C$.

It was a matter of considerable surprise to observe that the ferric hydroxide, completely precipitated by the effects of the first freezing process, should continue to exhibit such great ability (Table XIV) to prevent water from freezing.

The theoretical water curves have been included in Fig. 14. It will be seen that decreasing temperatures cause a gradual approach toward this line, as would be expected from the convergence of the temperature-lowering and -raising curves.

TABLE XIII

A Dilatometric Study of the Effect of Freezing upon the State of Water in a Colloidal Ferric Hydroxide Coagulum

	Sample I. 3.541 grams (water 84.22%)			Sample II. 2.7071 grams (water 85.25%)	
Remarks	Observed Temperature °C	Length of Capillary Toluene Column cm.	Remarks	Observed Temperature °C	Length of Capillary Toluene Column cm.
First freezing	0.0	0.00	First freezing	0.0	0.00
	− 4.0	− 0.70		− 6.0	− 1.60
	− 6.0	− 1.00		− 6.0	+18.25
	− 6.0	+25.55		− 8.0	+17.80
	− 8.0	+25.20		−12.1	+16.90
	−11.1	+24.80		−17.1	+15.75
	−16.1	+24.05		−25.0	+14.10
	−22.0	+23.20		−33.2	+12.10
	−29.0	+22.45		−28.0	+13.25
	−34.1	+21.80		−20.0	+15.45
	−39.9	+20.95		−12.1	+17.50
	−47.1	+19.80		− 6.0	+18.90
	−41.4	+20.90		−13.1	+17.50
	−35.8	+21.80		−21.0	+15.85
	−26.0	+23.30		−25.0	+14.90
	−19.0	+24.45		−15.2	+17.45
	− 9.1	+26.10	Thawed and refrozen 2nd freezing	−12.1	+17.80
	− 6.0	+26.60		−24.0	+15.00
				−35.0	+12.45
				−25.0	+15.10
				−16.1	+17.45
				− 6.0	+19.85
			Thawed and refrozen, 3rd freezing	−12.1	+17.95
				−23.0	+15.75
				−34.1	+12.95
				−26.0	+15.05
				−16.1	+17.50
				− 6.0	+19.85
			Thawed and refrozen, 4th freezing	−12.1	+17.95
				−22.0	+15.95
				−32.0	+13.40
				−25.0	+15.20
				−16.1	+17.45
				− 6.0	+19.75

TABLE XIV

A Calculation of the Percentage of the Total Water in Colloidal Ferric Hydroxide Systems which remained unfrozen when the System was cooled to Various Temperatures.   (Data calculated from Table XIII)

Sample	Remarks	Point of Initial Freezing		Temperature of Lowest Exposure	
		Temperature °C	Amount of "bound" water per cent	Temperature °C	Amount of "bound" water per cent
I	Temperature-lowering	− 6	18.07	−47	13.63
	Temperature-raising	− 6	14.85	−47	13.63
II	1st temperature-lowering	− 6	21.18	−33	17.22
	1st temperature-raising	− 6	19.00	−33	17.22
	2nd temperature-lowering	−12	17.02	−35	14.25
	2nd temperature-raising	−12	15.04	−35	14.25

Discussion

The Methods which were employed.—In our studies we have calculated a theoretical water curve, and in this calculation have ignored any contraction of ice upon subjecting it to decreasing temperatures.   This was done because it was possible to so nearly reconstruct the actually observed curve representing the freezing of 1.9550 grams of pure water (Fig. 2), without a consideration of the thermal expansion of ice.   If these water curves are erroneous, then the conclusions which have been drawn regarding the relation of observed volume increase to theoretical volume increase are in error.   However the disregarding of any slight volume change of ice with temperature change has no influence upon the further consideration given to the studies on gelatin and activated silica gel, by the establishment of a "corrected water curve." This correction has been made by allowing for the volume of toluene displaced by the mass of the dry solid used in preparing the colloidal system.   Obviously, with less toluene in the experimental system toluene-colloid-water than in the reference system toluene-water, the difference in quantity of toluene present must be considered, if the expansion or contraction of the volumes of the two systems are comparable when exposed to temperature change.

The Effect produced by Freezing upon Systems of the Elastic-Gel Type—(A) *Gelatin Gels.*—Under the experimental conditions of the present investigation, the freezing of the system gelatin-water was completely reversible.   These results are at variance with those reported by Molisch,[36] and by Fischer and Bobertag.[12]   They are also in opposition to the theoretical conclusions of

Kuhn,[29] and Stiles,[56] who considered that freezing would always be accompanied by a partial and a more or less permanent alteration of the original gel structure. The present study is in agreement with the results of Liesegang,[30] and Moran.[37]

Stiles[56] has emphasized the importance of the rate of freezing of colloidal systems in relation to the effects produced by the freezing process. He found that with thin sheets of hydrated gelatin the water-loss upon thawing was from 4 to 6 times greater from samples which had been slowly frozen, than from similar samples which had been frozen rapidly. Moran's[37] studies, demonstrating internal and external centers of ice crystal formation in gelatin gels, may be considered a verification and explanation of the results reported by Stiles. With the slowly frozen samples the ice formation was to a large extent external and as a consequence re-adsorption of the water was slow. On the other hand, Hardy[21] observed that when disseminated ice crystals formed *within* the gel, and when crystals of a solid solution of gelatin formed, the water resulting from thawing the frozen mass was immediately re-adsorbed.

Our experimental conditions favored rapid freezing of the gels. No permanent alteration of the gel has been observed, nor have studies under experimental conditions favoring slow freezing been made.

It should be stressed that when we refer to "an alteration of gel structure" it is with reference to a change in the gel structure of a behavior of the gel upon exposure to changing temperatures which is detectable and measurable by dilatometric technic. Thus in our system the gelatin gels occupied the same volume at any given temperature above 0°C after the sample had been frozen as had been occupied before freezing. Moran[37] believed that he could detect a slight volume change brought about by the process of freezing and thawing. Also, in our experiments the process of repeated freezing and thawing gelatin gels in no way altered the quantity of water which crystallized at the initial freezing point of the system. This has been interpreted as indicating that ice-crystallization took place relatively rapidly and that the centers of crystal formation were principally internal.

These results are considered as additional evidence in favor of the theory advanced in part by Hardy and in part by Fischer, Hardy postulating that dehydration could be considered a reversible process if a gel or sol resulted normally from the addition of a colloidal substance to water, and Fischer considering the process of freezing only a certain type of dehydration.

Moran, by means of the dilatometer, found that, with a 43.7% gelatin gel held at −11.0°C ice crystal formation was only complete after a period of twenty-six days. In view of his study it is pertinent to ask whether our results represent a true equilibrium of the freezing process. Our data designed to test this question indicate that our values cannot be greatly in error. The fact that it was possible to obtain results clearly demonstrating a reversible reaction with the elastic gels, is evidence that equilibrium must have been practically complete. Otherwise, a reading of the dilatometer at −15.0°C would have been distinctly different after exposure of the sample to a temperature of −50.0°C than before exposure to this lowered temperature.

We have already noted that our dilatometric data indicate that water-binding in gelatin gels is an adsorption reaction. Newton and Gortner[43] and Gortner[17] interpret water-binding in colloidal systems of gum acacia as an adsorption reaction, although this may not hold for all samples of gum acacia [cf. Newton and Martin[44]]. Further evidence of the nature of water-binding in hydrophilic colloidal systems is given by Newton and Martin.[44] Their gelatin data have been recalculated and are shown in Table XV and Fig. 15.
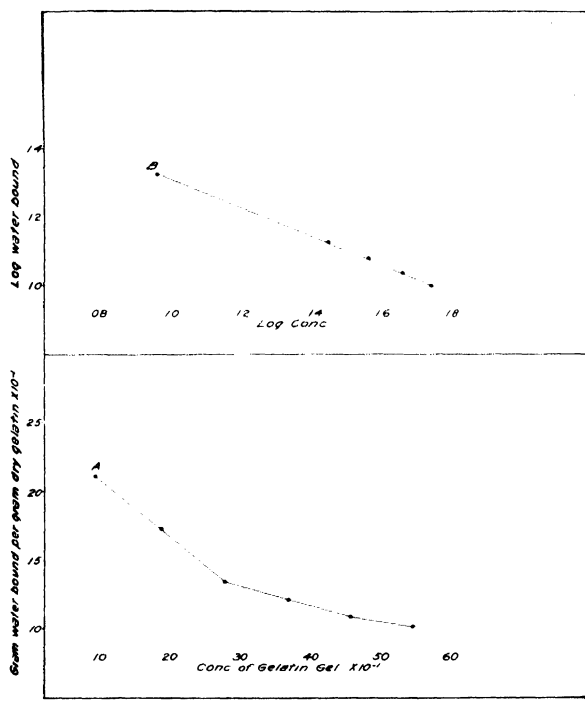
FIG. 15

Showing the weight of water bound by gelatin sols of different concentrations. Data expressed as grams water bound per gram dry gelatin (cryoscopic data of Newton and Martin).

TABLE XV

Bound Water in Gelatin Sols as a Function of the Concentration of the Gelatin Sol. Determinations by the Newton-Gortner Cryoscopic Method. Data of Newton and Martin[44]

Concentration of Gelatin in System per cent	Bound-Water per cent	Water Bound per Gram of Dry Gelatin grams
0.93	1.9	2.05
1.86	3.2	1.70
2.77	3.7	1.31
3.66	4.4	1.17
4.55	5.0	1.04
5.43	5.5	0.96

Newton and Martin's studies were carried out by the Newton-Gortner cryoscopic method, which can be used only with dilute gelatin sols, rather than gels. It will be seen that these data indicate again an adsorption reaction due to the fact that when the arithmetic values of gelatin concentration and bound water are plotted, Curve A, apparently a parabola, resulted, whereas when the logarithmic values were plotted a straight line relationship was indicated (Curve B). We have already (Fig. 8) shown a similar relationship from our dilatometric data.

A review of the literature on studies made upon aqueous gelatin-containing systems reveals a most interesting array of values for the actual quantity of water which is combined with gelatin or which exists in a "bound" condition.

The method of measurement of water-binding by gelatin has been different in nearly every study reported. Svedberg,[57] from studies upon the contraction of gelatin when wetted, considered the weight of water bound per gram dry gelatin to be in the neighborhood of 0.08 gram; Fischer, as cited by Moran,[37] from studies on the rate of drying found 0.1 gram water to be bound per gram dry gelatin. Taffel[58] considered the work of Sheppard and Sweet,[54] on the setting points of gels, as a basis for the value of 0.3 gram bound water per gram dry gelatin. Moran[37] from his dilatometric studies, found the value of 0.56 gram bound water per gram dry gelatin for gels of 43.7% and 52.1% concentration. Newton and Martin's results were obtained in a study of the freezing point depression of theoretically molar sucrose solutions.

With the technic of measurement of bound-water differing so radically, it is not surprising that different values were obtained for the quantity of water bound by a gram of gelatin. Furthermore, the concentration of the gelatin in the system is a factor which influences the value for weight of water bound per gram dry gelatin. This is clearly indicated by the results of the present study (see Table VIII and Fig. 8), and by the data of Newton and Martin (Table XV and Fig. 15). Our own data show that, in a system containing 2% gelatin at −10.0°C, 4.7 grams of water is "bound" per gram dry gelatin, while in a 32% gelatin gel at −10.0°C only 0.64 gram of water per gram dry gelatin appears to be "bound." This last value does not differ greatly from Moran's value which was also obtained by dilatometric studies.

From the standpoint that water-binding in gelatin gels appears to be an adsorption reaction, it was considered probable that the temperature at which the system would be frozen would influence the value for the quantity of water which was bound. However, no indication that temperature is a factor can be detected from an inspection of Figs. 3, 5 and 7, providing that sufficient time has elapsed for the establishment of an equilibrium in the freezing process. Over the temperature range which was studied, all of the water which could be frozen crystallized at the temperature of initial freezing and exposure of the system to decidedly lower temperatures was without effect upon the quantity of water which appeared to remain in the unfrozen condition.

A possible explanation may be that two factors are affecting the equilibrium (A) the vapor pressure of ice *decreasing* with lowering temperature and (B) an adsorption "pressure" *increasing* with lowering temperature. If the

increased adsorption tendency should be sufficient to just balance the lowered
vapor pressure of the ice, then the amount of "bound" water (adsorbed water)
should be a constant irrespective of temperature.

(B) *Systems of Fresh Egg White.*—With egg white, as with gelatin, the
freezing process appeared to be completely reversible. St. John[53] made a
study of bound-water in the thick portion of egg white, employing the method
of Rubner[52] as modified by Thoenes[60] and Robinson.[49] He found that at
− 5.0°C 85% of the water present appeared as bound-water, while at − 15.0°C
only 26% of the total water in the system appeared to be "bound." Our values
on a similar system are given in Table X. It is of interest to note that while
St. John's value at − 5°C is greatly in excess of our values at − 6°C (17.36%
and 20.18%) there is much less discrepancy at −15°C. Newton and Martin[44]
have also studied the question of bound water in fresh egg white, using a com-
posite sample from 16 eggs. In their studies the whites were beaten, allowed
to settle for 3.5 hours, the froth was removed, and the clear liquid underneath
taken for study. This clear liquid portion was then diluted to suitable con-
centrations. Bound water was measured by the Newton-Gortner cryoscopic
method. They found much lower values than either ourselves or St. John,
i.e., 0.7% bound water for a 2.37% sol, 2.3% for a 7.11% sol, and 6.5% for
an 11.85% (undiluted) sol. These values (recalculated) indicate respectively
0.29, 0.30, and 0.48 gram of bound water per gram dry albumin, whereas
using the dilatometric method we find (sample II at − 6°C) 1.55 grams of bound
water per gram dry egg white. These differences in the magnitude of the
values obtained by Newton and Martin and by ourselves are too great to be
explained wholly on the basis of the mechanical manipulation of the sample
or from the fact that their studies were made on a mixed sample of the thin
and thick portions of the white. Unquestionably the method by which bound
water is determined is the primary factor. Apparently a very considerable
fraction of the "bound" water as measured by dilatometric and (probably
calorimetric) technics can act as a solvent for sucrose and thus lead to low
values when the Newton-Gortner cryoscopic method is employed. Further
studies of this colloidal system must be made before final conclusions can
be drawn.

The Effect produced by freezing Systems of the Inelastic-Gel Type.—Pulverized
activated silica gel proved to be very desirable material for bound-water
studies. It was sufficiently granular to wet readily, was very stable in nature,
and in repeated and consecutive determinations gave readily duplicable results.
Thus, the water "frozen out" by temperatures decidedly lower than the initial
freezing point was completely re-adsorbed when the sample was thawed. This
ability to return after the freezing cycle to the condition existing before freez-
ing occurred was not observed by us in other inelastic-gel systems. At no
point in the recorded temperature study did we observe a temperature below
which no more water would freeze if the temperature were lowered further.
Possibly all the water added to these samples would freeze if sufficiently low
temperatures were employed. If this be true, then water in the silica gel
system may exist only as "free-water" and "capillary-water." All the water

which failed to freeze at the point of initial freezing might be classed as "apparent capillary-water" at this temperature. The true measure of "capillary-water" would then be all the water which did not freeze at the initial freezing point of the system. This point in the present studies appears to lie between $-1.0°C$ and $-2.0°C$.

It is apparent, however, from Table XII that the system would have to be exposed to extremely low temperatures in order to freeze all of the water, since the "bound water" (i.e. water not frozen) values decrease very slowly with lowering temperature. Thus in the 60% gel the "bound water" has decreased only from 29.9% to 22.9% in the range $-10°C$ to $-48°C$ and in the 80% gel from 38.32% to 27.58% in the same temperature range. An extrapolation of the curves for "bound water" indicates that all of the water would not be frozen until the sample had been exposed to temperatures below $-80°C$.

Ferric hydroxide gels exhibited a behavior similar to that of silica gel. A certain portion of the total water content froze at a constant temperature and the remaining quantity of unfrozen water gradually decreased as the temperature was lowered.

Although the freshly prepared ferric hydroxide system possessed a marked degree of rigidity, the structure was readily altered by freezing. The actual affinity for water, in the ferric hydroxide coagulum, seemed to be reduced but little by freezing, but the dispersion of the particles was permanently altered. That this alteration can be the result of the disruption of capillary spaces seems unsupported by the observed behavior. If the capillaries had been so completely injured by the freezing process, it would seem that the water-binding property of the colloidal system should have been materially decreased. Apparently the freezing process has in some manner produced an agglomeration of the colloidal particles, with no great effect upon the capillarity of the substance. The first freezing cycle (Sample II) reduced the apparent "bound" water at $-6°C$ from 21.18% to 19.00%. A second freezing cycle reduced this only slightly and two additional freezing cycles were practically without effect insofar as reducing the amount of "bound" water is concerned.

In the activated silica gel studies, no apparent disruption of the capillaries occurred, as is evidenced by the duplicability of the dilatometer readings upon repeated freezing and thawing. Foote and Saxton (13) report similar findings and note that this behavior of a silica gel system is not paralleled by the behavior of aluminum and ferric hydroxide gels.

The General Behavior of Aqueous Colloidal Systems upon Exposure to Low Temperature.—It is widely accepted that with aqueous colloidal systems there is a definite temperature, below the freezing point of the system, at which all of the "free-water" will be frozen. This conception is held especially in the field of biological investigation. With biological material this temperature has been arbitrarily selected as about $-20.0°C$ [Rubner,[52] Thoenes,[60] Robinson[48,49,50]], apparently on the assumption that all of the "free" water would be frozen at this temperature and that the temperature was not sufficiently low to seriously alter the free-bound water ratio.

Our experimental data indicate that all temperatures below that of the initial freezing of systems of gelatin-water are temperatures at which all of the "free-water" but none of the "bound-water" is frozen. With the inorganic hydrogels there was no temperature within the range of $0.0°C$ to $-50.0°C$ at which a lower temperature did not cause the crystallization of additional quantities of ice.

Additional studies must be carried out before generalizations can be made as to the behavior of other aqueous colloidal systems upon exposure to low temperature. It seems probable, however, that biological tissue and related systems would behave more nearly like the gelatin system than silica or ferric hydroxide gels.

The results of this study further emphasize the importance of the length of the time interval during which the freezing of a colloidal system takes place. At temperatures decidedly lower than the freezing point of the system, the gel-ice equilibrium is rapidly established. At temperatures near the freezing point of the system the slow rate of ice formation is responsible for the slow establishment of phase equilibrium.

Summary

1. Dilatometric studies have been made of the state of the water in certain aqueous colloidal systems as affected by exposure to temperatures ranging from $0.0°C$ to $-50.0°C$. The systems studied were: gelatin gels of different concentrations, the thick portion of egg white from fresh eggs, mixtures of different concentrations of activated silica gel and water, and hydrated ferric hydroxide.

The low temperatures utilized in these studies were easily produced and maintained by proper mixtures of alcohol and solid carbon dioxide. The temperatures noted were measured by means of a standardized thermometer.

2. The colloidal systems studied fall into two general classes: (a) those in which the freezing process is completely reversible; and (b) those in which the freezing is an irreversible or only partially reversible process.

3. In the studies made upon gelatin it has been found that all the water which could be frozen within the temperature range of $0.0°C$ to $-50.0°C$ was frozen at the recorded initial freezing temperature (approx. $-6°C$) if sufficient time was permitted for establishment of equilibrium. After equilibrium establishment at this point, exposure to much lower temperatures was without effect upon the quantity of water which remained in the unfrozen condition ("bound" water).

4. The rate of establishment of ice-gel equilibrium was found to be very slow, the rate being influenced greatly by (a) the concentration of the gel, and (b) the temperature of exposure. This fact emphasizes the importance of the consideration of time as a factor influencing the quantity of water which will be frozen at any given temperature.

5. Water-binding in the system, gelatin-water, appears to be an adsorption reaction. A logarithmic relationship was found to exist between the con-

centration of the gelatin gel and the grams of water which were "bound" per gram dry gelatin. In our studies 0.70 gram of water was "bound" per gram dry gelatin in a 32% gelatin gel and 4.675 grams of water per gram dry gelatin were "bound" in a 2% gelatin gel.

6. The freezing behavior of the thick portion of fresh egg white appears to be a completely reversible process, in this respect paralleling the gelatin systems.

7. The form and the slope of the dilatometric curves indicated that no disruption of capillary spaces in silica gel occurred when silica gel-water systems were frozen. The freezing of colloidal ferric hydroxide resulted in a relatively small decrease in "capillary water."

8. The quantity of "capillary-water" which could be frozen from ferric hydroxide and activated silica gel was proportional to the temperature at which the sample was exposed. With ferric hydroxide and with 25% activated silica gel mixtures, this quantity of "capillary-water" frozen appeared to be directly proportional to the lowering of the temperature. With 60% and 80.5% mixtures of activated silica gel this relationship held approximately to temperatures as low as $-30°C$. At temperatures lower than $-30.0°C$ "capillary-water" froze at a more rapid rate than at temperatures above this point.

9. It is postulated that the effect of freezing upon colloidal ferric hydroxide and similar substances is to cause in some manner an agglomeration or flocculation of the colloidal particles without materially reducing the capillarity exhibited by the substance.

10. The dilatometric method has proven a useful technic for "bound" water studies. The values for "bound" water which we have obtained in our work appear to approximate the values obtained by other workers using Rubner's (Thoenes) calorimetric method on similar materials.

11. It is emphasized that "bound" water is an indeterminate term, and that "bound" water values as experimentally determined may be expected to vary from system to system, the variation being due to many factors, not the least of which is the method selected for measurement. If biological cells and tissues are similar in their behavior to gelatin and (probably) to the thick portion of egg white, then "bound" water is a measurable entity and (using dilatometric procedure) has a constant value at least at temperatures between $-6°$ and $-50°C$.

Literature cited

[1] A. T. Barnes: Colloid Symposium Monograph, **3**, 103-111 (1925). Colloidal Water and Ice.

[2] O. Bobertag, K. Feist and H. W. Fischer: Ber., **41**, 3675-3679 (1908). Über das Ausfrieren von Hydrosolen.

[3] G. J. Bouyoucos: J. Agr. Res., **8**, 195-217 (1917). Measurement of the Inactive or Unfree Moisture in the Soil by Means of the Dilatometer Method.

[4] G. J. Bouyoucos: Mich. Agr. Expt. Sta. Tech. Bull. No. **36**, (1917). Classification and Measurement of the Different Forms of Water in the Soil by means of the Dilatometer Method.

[5] D. R. Briggs: J. Phys. Chem., **36**, 367 (1932).

[6] G. Bruni: Ber., **42**, 563-565 (1909). Über das Ausfrieren von Gallerten.

[7] E. H. Callow: Proc. Roy. Soc., **108A**, 307-323 (1925). Ice Crystallization through Super-cooled Gelatin Gels.

[8] J. W. Crist: Mich. Agr. Expt. Sta. Tech. Bull. No. **74** (1926). Effect of Nutrient Conditions on Colloidal Properties of Certain Vegetable Crops.

[9] S. Dunn: Science, (2) **69**, 359-360 (1929). Carbon Dioxide Ice as a Laboratory Refrigerant.

[10] H. A. Fells, and J. B. Firth: J. Phys. Chem., **31**, 1230-1236 (1927). Function of Water present in Silicic Acid Gel. Structure of Silicic Acid Gel.

[11] H. W. Fischer: Kolloid-Z., **8**, 291-302 (1911). Das Wasser im Plasma.

[12] H. W. Fischer and O. Bobertag: Biochem. Z., **18**, 58-94 (1909). Über das Ausfrieren von Gelen.

[13] H. W. Foote and B. Saxton: J. Am. Chem. Soc., **38**, 588-609 (1916). The Effect of Freezing on Certain Inorganic Hydrogels.

[14] H. W. Foote and B. Saxton: J. Am. Chem. Soc., **39**, 627-630 (1917). The Freezing of Water absorbed in Lamp Black.

[15] H. W. Foote and B. Saxton: J. Am. Chem. Soc., **39**, 1103-1125 (1917). The Effect of Freezing on Certain Inorganic Hydrosols.

[16] H. Freundlich: "Colloid and Capillary Chemistry" (1926).

[17] R. A. Gortner: "Outlines of Biochemistry" (1929).

[18] R. A. Gortner: Trans. Faraday Soc., **26**, 678-686 (note especially the appended "Discussion" pp. 686-704) (1930). The State of Water in Colloidal and Living Systems.

[19] W. B. Hardy: J. Phys. Chem., **4**, 235-253 (1900). The Conditions which determine the Stability of Irreversible Hydrosols.

[20] W. B. Hardy: J. Phys. Chem., **4**, 253-273 (1900). On the Mechanism ot Gelation in Reversible Colloidal Systems.

[21] W. B. Hardy: Proc. Roy. Soc., **112A**, 47-61 (1926). A Microscopic Study of the Freezing of a Gel.

[22] J. A. Harris, *et. al.* Unpublished work. Cited by Gortner (16) p. 235.

[23] A. V. Hill: Proc. Roy. Soc., **106B**, 477-505 (1930). The State ot Water in Musc'e and Blood and the Osmotic Behavior of Muscle.

[24] A. V. Hill and P. S. Kupalov: Proc. Roy. Soc., **106B**, 445-477 (1930). The Vapor Pressure of Muscle.

[25] International Critical Tables, **3**, 27-29 (1928).

[26] International Critical Tables, **3**, 43 (1928).

[27] H. R. Kruyt: "Colloids" (1929).

[28] H. R. Kruyt and K. C. Winkler: Z. anorg. allgem. Chem., **188**, 200-204 (1930). Über den Einfluss hydratierter Kolloide auf die Gefrierpunktserniedrigung.

[29] A. Kuhn: Kolloid-Z., **35**, 275-294 (1924). Überblick unser jetzigen Kentnisse über Wasserbindung in Kolloiden.

[30] R. E. Liesegang: Kolloid-Z., Flora, **96**, 523-524 (1906). Über das Erfrieren der Pflanzen.

[31] R. V. Lott: Mo. Agr. Expt. Sta. Rsh. Bull. No. 95. Correlation of Chemical Composition with Hardiness in Brambles.

[32] A. Lottermoser: Ber., **41**, 3976-3979 (1908). Über das Ausfrieren von Hydrosolen.

[33] M. H. McCool and C. E. Millar: Bot. Gaz., **70**, 317-319 (1920). Use of the Dilatometer in studying Soil and Plant Relationships.

[34] J. McGavack and W. A. Patrick: J. Am. Chem. Soc., **42**, 946-978 (1920). The Adsorption of Sulfur Dioxide by the Gel of Silicic Acid.

[35] J. H. Martin: J. Agr. Res., **35**, 493-535 (1927). Comparative Studies of Winter Hardiness in Wheat.

[36] H. Molisch: "Untersuchungen über das Erfrieren der Pflanzen" (1897); Sitzungsber. Akad. Wiss. Wien, **105**, Abt. 1 (1896). Das Erfrieren von Pflanzen bei Temperaturen über dem Eispunkt. Cited by H. W. Fischer. (11). Originals not seen.

[37] T. Moran: Proc. Roy. Soc., **112A**, 30-46 (1926). The Freezing of Gelatin Gel.

[38] Müller-Thurgau: Landw. Jahrb., **9**, 133-189 (1880); **15**, 453-610 (1886). Über das Gefrieren und Erfrieren der Pflanzen.

[39] R. Newton: Univ. Alberta Agr. Rsh. Bull., No. 1 (1923). The Nature and Practical Measurement of Frost Resistance in Winter Wheat.

[40] R. Newton: J. Agr. Sci., **12**, 1-19 (1922). A Comparative Study of Winter Wheat Varieties with Especial Reference to Winter Killing.

[41] R. Newton: J. Agr. Sci., **14**, 178-191 (1924). Colloidal Properties of Winter Wheat Plants in Relation to Frost Resistance.

[42] R. Newton and W. H. Cook: Canad. J. Res., **3**, 560-578 (1930). The Bound Water of Wheat-Flour Suspensions.

[43] R. Newton and R. A. Gortner: Bot. Gaz., **74**, 442-446 (1922). A Method for estimating the Hydrophilic Colloid Content of Expressed Tissue Fluids.

[44] R. Newton and W. McK. Martin: Can. J. Res., **3**, 336-427 (1930). Physico-Chemical Studies on the Nature of Drought Resistance in Crop Plants.

[45] F. W. Parker: J. Am. Chem. Soc., **43**, 1011-1018 (1921). The Effect of Finely Divided Material on the Freezing Points of Water, Benzene and Nitro-Benzene.

[46] W. A. Patrick and N. F. Eberman: J. Phys. Chem., **29**, 220-228 (1925). Studies in Adsorption from Solutions from the Standpoint of Capillarity. II.

[47] W. A. Patrick and D. C. Jones: J. Phys. Chem., **29**, 1-10 (1925). Studies in the Adsorption from Solution from the Standpoint of Capillarity. I.

[48] W. Robinson: J. Econ. Entom., **20**, 80-88 (1927). Water-Binding Capacity of Colloids, A Definite Factor in Winter Hardiness of Insects.

[49] W. Robinson: Colloid Symposium Monograph, **5**, 199-218 (1928). Relation of Hydrophilic Colloids to Winter Hardiness of Insects.

[50] W. Robinson: J. Econ. Entom., **21**, 897-902 (1928). Water Conservation in Insects.

[51] J. T. Rosa, Jr.: Mo. Agr. Expt. Sta. Rsh. Bull., **48**, (1921). Investigations on the Hardening Process in Vegetable Plants.

[52] M. Rubner: Abh. preuss. Akad. Wiss., Phys.-Math. Klasse, **1922**, 3-70. Über die Wasserbindung in Kolloiden mit besonderer Berücksichtigung des quergestreiften Muskels.

[53] J. L. St. John: Unpublished Ms. Bound Water in Hydrophilic Colloids.

[54] S. E. Sheppard and S. Sweet: J. Ind. Eng. Chem., **13**, 423-424 (1921). The Setting and Melting Points of Gelatins.

[55] S. P. L. Sörensen: Compt. rend. trav. lab. Carlsberg, **12**, 164-212 (1917). Studies on the Proteins.

[56] W. Stiles: Food Investigation Board. Special Report No. 7. London, H. M. Stationery Office. (1922). The Preservation of Food by Freezing, with Special Reference to Fish and Meat: A Study in General Physiology.

[57] T. Svedberg: J. Am. Chem. Soc., **46**, 2673-2676 (1924). Density and Hydration in Gelatin Sols and Gels.

[58] A. Taffel: J. Chem. Soc., **121**, 1971-1984 (1922). Thermal Expansion of Gelatin Gels.

[59] G. Tammann: Z. physik. Chem., **23**, 326-328 (1897). Über die Erstarrungsgeschwindigkeit. (cf. also J. Friedlander and G. Tammann: Z. physik. Chem., **24**, 152-159 (1897)). Über die Krystallisationsgeschwindigkeit; G. Tammann: "Kristallisieren und Schmelzen," 131-148. (1903).

[60] F. Thoenes: Biochem. Z., **157**, 174-176 (1925). Untersuchungen zur Frage der Wasserbindung in Kolloiden und tierischen Geweben.

[61] J. H. Walton and A. Brann: J. Am. Chem. Soc., **38**, 317-330 (1916). The Effect of Dissolved Substances on the Velocity of Crystallization of Water.

[62] B. L. Vanzetti: Atti. Inst. Veneto, Sci., **75**, 261 (1915); **76**, 287 (1916). Cited by Fells and Firth: J. Phys. Chem., **31**, 1231 (1927). (Original not seen).

[63] Vogel: Gilbert's Ann. Physik., **46**, 137 (1820). Über die Veränderung, welche einige Stoffe des organischen Reiches beim Gefrieren erfahren.

Division of Agricultural Biochemistry,
University of Minnesota,
St. Paul, Minnesota.

THE STRUCTURE AND ELECTRICAL PROPERTIES OF INSULATING MATERIALS

BY JOHN WARREN WILLIAMS

The importance of making available information concerning the chemical structure of commercial dielectrics is becoming increasingly evident as the mechanisms of conduction and loss of energy in them are being described. These mechanisms usually depend upon the presence of ions, either free or adsorbed, but may also sometimes depend upon the presence of polar molecules if alternating current behavior is being studied.

Important engineering studies of the electrical characteristics of solid and liquid dielectrics have been made in recent years and it can be said that in general the difficulties due to lack of exact chemical knowledge of the materials have been recognized. For example, crystals have been subjected to test because of their relative freedom from impurities, and the breakdown processes in highly purified liquids such as hexane, heptane and xylene have been carefully investigated. The highly purified liquids behave quite differently from the ordinary insulating oils in that the latter always show a residual conductivity, which, incidentally, has been traced to the presence of colloidal particles in the oils.

The belief seems to be growing that in most solid dielectrics the conduction of the electric current does not take place uniformly through the material as a whole but rather along paths of higher conductivity. In the case of crystalline dielectrics in which there are ionic conductors Smekal[1] believes that the mechanism of electrical conductance is essentially bound up with the deviation of the actual crystal structure from that of the ideal lattice. The ions which take part in conduction are assumed to be concentrated in positions in the crystal where these lattice imperfections are present and move in an adsorbed condition along the paths formed by these crystalline fissures. Smekal has estimated that the ideal part of the lattice in a crystal unit contains something of the order of magnitude 10^4 to 10^5 atoms so that the "mosaics" or blocks are truly colloidal in dimension. This idea of Smekal has found favor with many investigators who have studied the electrical properties of crystals and it is supported by others in their considerations of the thermal, optical and mechanical properties of these materials. It has been considered favorably in an interesting article by Murphy and Lowry[2] on the complex nature of dielectric absorption and dielectric loss.

While such a mechanism is questionable in the case of crystalline substances it appears to give a correct description of the conduction processes taking place in such moisture absorbing dielectrics as cellulose, cotton, silk, rubber, the resins, and other similar and related materials. The ability of

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[1] Z. Elektrochemie, **34**, 472 (1928); Ann. Physik, (4) **83**, 1202 (1927).

[2] J. Phys. Chem., **34**, 598 (1930).

forms of these solids to give definite and interpretable X-ray diagrams, obser-
vations concerning the manner in which they swell in suitable solvent media,
the viscosity of their solutions and their ability to form homogeneous films on
water and mercury all indicate what may be termed a fiber-like structure
for them.

A number of theories have been proposed to explain the mode of formation
of these substances which for purposes of discussion will be classified as gels or
as highly polymerized organic substances. It is more or less generally agreed
that they are heterogeneous in the sense that there is present both a continuous
and a disperse phase, with the two phases forming a network. Studies of their
elasticity and rigidity can best be interpreted on the assumption that the dis-
perse phase is made up of particles which have aggregated to form chains or
fibrils which will be arranged regularly in some cases and randomly in others.
But although the existence of these chains had been suspected for many years
it is not until rather recently that their existence seems definitely established.

Discussion with regard to the actual constitution of these high molecular
(or aggregate) weight compounds has centered around two theories known in
the literature as the association theory of Hess and Pringsheim and the
macromolecular theory of Staudinger. In the association theory smaller
molecular units or residues are held together to form the aggregates through
secondary valences, while in the macromolecular theory the fundamental
groups are chains or fibrils of such residues which are held together by primary
valence forces. Their lengths, molecular weight and other physical properties
will depend upon the degree of polymerization or condensation, while their
chemical properties will depend in a large measure upon the groups which
happen to be present at the end of the chains. We shall favor the explana-
tion of the macromolecular theory in this article.

It has been mentioned that the results of a number of physical studies on
cellulose, silk, tissue and stretched rubber indicate the presence of long primary
valence chain macromolecules. In the space available it will not be possible
to completely outline these results, but the manner in which they have been
obtained may be suggested. Foremost among them are the X-ray diffraction
studies which have been made by Meyer and Mark, Hengstenberg, Sponsler
and Dore, Herzog and Jahnke, Polanyi, Weissenberg, Clark, Hauser, and
others. The point of view has gradually developed that it is not necessary, as
had previously been believed, for the unit crystal cell to contain an integral
number of whole molecules or its equivalent in ions. In the substances with
distinctly fibrous structure the chains linked by primary valences pass through
the unit cell in such a way that only two links in each chain are found in the
unit crystal cell. The macromolecules themselves have been shown to be
sometimes as long as 500 Å while the single molecular units from which the
chain is formed will be of the order of magnitude of 10 Å in height. In
cases where the chains are built in spiral form one complete turn is indicated
by a distinctive periodicity in the X-ray diagram from which the height of
the unit cell is defined. A certain number of these chains are held together
by the secondary valence forces to form bundles or micelles. The micelles are

probably held together by means of amorphous cementing materials which would be called the dispersion medium in the language of colloid chemistry. Of course the micelles will not always be oriented with their long dimension parallel (or nearly so) to the fiber axis but it is perhaps surprising how common this arrangement is. It has been established for cellulose, silk, tissue, stretched rubber, stretched gelatin and certain of the silicates.

It is not difficult to demonstrate that the forces acting in a direction parallel to the chains are much stronger than those acting perpendicular to them. In those cases where the micelles are already oriented, the fibers subjected to tensile strength tests are very strong in the direction of the fibers and much weaker in other directions. Measurements of the coefficient of expansion in the different directions also indicate the presence of this orderly arrangement.

Parallel and random arrangements of the micelles may also be differentiated by experiments in which the swelling of the materials is studied. When a section of regular arrangement swells it expands at right angles to the direction of the fibers but is not elongated. On the other hand, a section built of micelles arranged in random fashion swells not only uniformly but also much more rapidly. In the oriented structures the micelles are more tightly packed and liquids penetrate more slowly.

One of the most difficult points in connection with these theories has been the explanation of the nature of the secondary valence forces in these high molecular weight substances. In the cases where it has been possible to obtain X-ray diagrams it appears that two carbon atoms joined by the primary valences are separated by a distance of 1.5 to 1.6 Å, and the carbon to nitrogen distance of separation is perhaps 10% less. In the case of the macromolecular theory of the composition of these materials it is assumed that the primary valence bonds act in the direction of the chains so that their strength for directions other than parallel to these chains must be explained. This may be accomplished according to Meyer and Mark[3] by assuming the secondary valences to be cohesive forces of a van der Waals nature acting between atoms in different chains which will be separated by distances of the order of magnitude 4 Å. We could be more satisfied with this explanation if the mechanism of these forces could be more exactly described. The existing classical theories we owe to Debye[4] and Keesom[5] who have assumed them to be due to the electrostatic action of fixed dipoles or quadrupoles, and to the modification of existing dipoles by a distortion effect. In the case of interaction between fixed dipoles the forces will diminish with increasing temperature but in the case of induced dipoles the effect will be independent of temperature, according to the now well known dipole theory of Debye. The method of the theories has been to calculate the dipole and quadrupole moments from known values of the van der Waals constant. However, it appears from quantum mechanical calculations[6] too recent to be included in the book of Meyer and Mark that

[3] "Der Aufbau der hochpolymeren organischen Naturstoffe" (1930).

[4] Physik. Z., 21, 178 (1920); 22, 302 (1921).

[5] Physik. Z., 22, 129 (1921).

[6] Eisenschitz and London: Z. Physik, 60, 491 (1930); London: 63, 245 (1930).

hydrogen has a quadrupole moment which according to the classical theory would have given a value of the van der Waals constant which is much too low. Therefore, these theories are in need of some revision. The method of the new theory is to take the mutual perturbations of the periodic electronic motions into account with the result that there may be calculated both the primary and secondary valence forces for very simple molecules. The primary forces act over very short distances only (order of magnitude 1.5 Å) but the van der Waals or secondary forces diminish with distance much less rapidly and in addition the magnitudes of the latter seem to be of the right order of magnitude. It still remains to be seen whether or not this kind of calculation can be extended to the complicated systems under discussion.

It is desired to ascertain whether or not the electrical properties of these materials will depend upon their capillary structure. The results of a number of investigations have shown that the conduction of the electric current by these substances is not due to moisture condensed on outside surfaces but takes place because of the presence of moisture and ionizable materials in them. The form of conductance vs. electrolyte content and conductance vs. moisture content curves may be considered proof of this statement. An excellent example of the effect of the presence of ionizable materials is shown in the recent studies of Kemp[7] who has demonstrated that if rubber is purified with respect to the nitrogenous constituents always present its electrical characteristics may be considerably improved. Textile materials to be used as covering for wire are now washed in water to remove inorganic impurities.

It is suggested here that the conductance is determined by the capillary structure of the insulating materials, it being due to the ionic processes operating between individual fibers or chains. The objection may be raised that such an ionic process in conducting paths makes the presence of the complex electric currents which are always found in these substances impossible of explanation. The interionic attraction theory of electrical conductance now widely accepted indicates that free ions such as exist in the conducting paths of moisture absorbing dielectrics should behave to some extent like a dielectric, owing to the ionic atmosphere surrounding each ion. The free ions then carry not only the ordinary conduction current but also a complex current with its displacement current and conduction current components. Also in addition to the constant conduction current with its I^2R heat loss free ions may produce dielectric loss in cases where the resistance of the path is variable, and conducting paths instead of being pure resistances become equivalent to resistance in series with a condenser, giving a greater alternating current conductance. Ions, in addition to being free, may be adsorbed along the conducting paths. If these ions are at all mobile they may oscillate due to an impressed alternating field giving rise to a corresponding absorption of energy. Such a movement of ions may in certain cases be equivalent to a condenser charging and discharging current.

Any mechanism which describes the process of conduction in a dielectric must account for the fact that the conductivity is increased when the strength

[7] Bell System Tech. J., **10**, 132 (1931).

of the applied field is increased. In this case it seems reasonable to assume that the effect of increased voltage will be to increase the number of dissolved ions because those least strongly adsorbed will be set free to carry the current in the ordinary ways. Another possible explanation of the effect produced by the use of high field strengths may be found in the deviations from Ohm's Law first observed by Wien[8] and explained by Joos and Blumentritt.[9] To discuss this effect we shall have to describe the ionic atmosphere more exactly. According to the newer theories dealing with the behavior of strong electrolytes in dilute aqueous solution only ions are present, furthermore, since Coulomb's Law is assumed to express the forces between them, there will be more ions of unlike than of like sign around a given ion, in other words any given ion will in effect be surrounded by a kind of space lattice arrangement of oppositely charged ions called its ionic atmosphere. It is similar in all respects to the double layer so commonly referred to in colloid chemistry. This atmosphere has a radius which may be calculated and it requires a definite time to be either formed or destroyed. Furthermore, it will always be symmetrically built about a stationary ion. But because of its finite time of relaxation the atmosphere can no longer be built symmetrically if the ion is caused to move and it will become unsymmetrical in the direction of the motion. Before the ion there will be more ions of like charge and behind it more ions of opposite charge so that each moving ion, positive or negative, is subjected to a force which decreases its mobility. If we consider an interval of time over which the atmosphere can be regarded as relatively stationary, and if during this interval the ion is removed to a distance much greater than the thickness of the atmosphere, the influence of the latter will become small and we are left with an increased conductance because the interionic forces which decrease the ionic mobilities have been overcome.

Gemant,[10] in a recent book, has suggested an explanation of the effect of high field strengths which is quite different. Accordingly to this investigator it seems more logical to assume that undissociated molecules may also take part in the conduction, their decomposition being caused by the attraction of the poles for the several parts of the molecule.

It has been noted that Smekal and others believe the conduction in crystals to be due to the presence of lattice imperfections in which the ions move in an adsorbed or free condition along paths formed by these fissures and that the Smekal point of view is supported by indirect evidences provided by the mechanical and optical properties of crystals. However, the writer believes the conductance in these systems to be a volume process of the normal ionic type in which the dielectric losses can be accounted for by the Joule heat law. This conclusion has been previously drawn by Joffé,[11] Phipps,[12] and by others. In the first place Joffé has shown that a crystal has a characteristic specific

[8] Ann. Physik, (4) **83**, 327 (1927); **85**, 795 (1928).
[9] Physik. Z., **28**, 836 (1927).
[10] "Elektrophysik der Isolierstoffe" (1930).
[11] "The Physics of Crystals" (1928).
[12] Phipps, Lansing and Cooke: J. Am. Chem. Soc., **48**, 112 (1926).

conductance, that is, its conductance is a property of the chemical substance (KCl, SiO₂ etc.) rather than of the crystal and it is independent of crystal imperfections. This conclusion could be drawn only after the most extensive purifications of the crystals had been carried out.

According to this point of view, the electrical conductance of a solid salt depends only upon the number of free ions in the lattice at the given temperature. Furthermore, if the logarithm of the specific conductance is plotted against the reciprocal of the absolute temperature, a straight line is obtained which is of great significance. This has been expressed in the following way by Phipps:

$$\frac{d \ln k}{dT} = \frac{q}{RT^2}$$

$$\ln k = -\frac{q}{RT} + c.$$

where k is the specific conductance of the crystal
      T is the absolute temperature
      R is the gas constant
      c is a constant
  and q is the heat of liberation of a gram ion in the crystal lattice, that is, the work necessary to produce a mole of ions in the interior of a crystal.

It is peculiar to these systems that frequently only one kind of the ions is liberated and they carry all of the current. In a series of simple salts with a common anion, the chlorides of K, Ag, Na, etc., in which the positive ion is the carrier, the slopes of the ln k vs. $1/T$ curves will all be equal. In other words the energy necessary to liberate a positive ion from a chloride lattice is always the same.

If, on the other hand, one deals with a series of simple salts with a common cation, NaF, NaCl, NaBr, and NaI, it is found that the slope of the curve becomes progressively less in the order given, indicating that the energy necessary to liberate Na^+ ions becomes less the greater the atomic weight of the anion. The work of liberation of an ion is also related to other properties. The following table, adapted from the article of Phipps, Lansing and Cooke, shows it to be closely related to the natural quantum of the crystal as derived from specific heat data.

TABLE I

Relation between Heat of Liberation of a Gram Ion and the
Natural Quantum of the Lattice

Crystal	q (cals)	q/hν
NaF	32,800	38.2
NaCl	20,200	36.4
NaBr	18,400	42.4
NaI	13,800	38.5

The following sentence is quoted from the article of Phipps, Lansing and Cooke. "As the heat of liberation decreases the quantum of energy decreases correspondingly, so that the number of quanta necessary to activate the Na^+ ion is practically constant for such a series."

The observed conductance effect is not a dielectric displacement (except possibly at very low temperatures), because in that event the effect would change but little with temperature. The current actually transfers charges through distances incomparably greater than atomic and molecular distances. Another important fact to be considered is that many experiments of Joffé and of Tubandt[13] have shown Faraday's Law of electrolysis to be quantitatively obeyed.

It can be predicted that with a systematic study the number of quanta required to activate the several ions will in each case be constant, that periodic regularities will appear, and further that the laws based upon an ionic conduction in a homogeneous medium will be obeyed. In other words, the electrical behavior of a crystal appears to be quite different from that of the type of substance which has been described as a moisture absorbing dielectric, although many believe the mechanisms in the two cases to be quite similar.

In order to definitely decide such questions as have been discussed, it seems necessary to continue the careful studies of the compositions, sizes and shapes, and arrangements of the aggregated molecules which form the highly polymerized organic substances. It is of more than passing interest that as these scientific problems are being solved, means are indicated by which the electrical characteristics of our ordinary dielectric materials may be improved.

Laboratory of Colloid Chemistry,
University of Wisconsin,
June 1, 1931.

Z. anorg. Chem., **115**, 105 (1921), et. al.

INDUCED OXIDATION OF GLUCOSE IN PRESENCE OF INSULIN ACTING AS AN INDUCTOR

BY HIRA LAL DUBE AND N. R. DHAR

In previous papers[1] we have advanced the view that insulin acts as a promoter in the oxidation of glucose in the animal body. The experimental results recorded in this paper shows that *in vitro* insulin acts as an inductor in the oxidation of glucose in presence of phosphates by passing air, although Spoehr and Smith[2] did not observe any increased oxidation of glucose in presence of insulin. The experimental details are not available in the paper of Spoehr and Smith.

All our experiments were carried out in diffused daylight inside the room at a temperature of about 25°. In these experiments a slow current of air was passed through a series of bottles, containing 20% sodium hydroxide solution, baryta and concentrated sulphuric acid to free the air from carbon dioxide gas and moisture. This carbon dioxide free air was passed through the solution of glucose containing insulin and other substances, such as ferrous hydroxide, sodium phosphate, etc. A measured volume of air was passed. The insulin used was obtained from British Drug House, containing 5 cc. in the tube and 1 cc. contained 20 units. In every experiment a fresh solution of the insulin was taken, as it was observed during the experiments that the solutions putrifies on keeping. It is practically neutral and does not reduce Fehling's solution. 5 cc. of the insulin (20 units) in the tube was made up to 50 cc. by adding distilled water and this aqueous insulin was used in the following experiments. Extra pure glucose of Merck was used for the experiments. The volume of the solution to be oxidized was always made up to 100 cc. by adding distilled water. 36.5 litres of air were passed in 15 hours.

Experiments with Insulin and Sodium Phosphate

In each of these experiments 10 cc. of 1% glucose solution was taken and it was estimated by the reduction of Fehling's solution and finally weighing the precipitate as cupric oxide.

$$10 \text{ cc. glucose} = 0.2310 \text{ gram } CuO.$$

In the following experiment 0.348 N solution of disodium hydrogen phosphate was used:

No. of experiment	Litres of air passed	Insulin in cc.	Sodium Phosphate in cc.	Actual weight of glucose in 10 cc. of the solution taken in grm. (Blank)	Amount of glucose left after experiment in grm.	Amount of glucose oxidised in grm.	Percentage amount of glucose oxidised
1	36.5	10	10	0.1000	0.0982	0.0018	1.8

[1] Dhar: Chemie der Zelle und Gewebe, **12**, 217 (1925); J. Phys. Chem., **29**, 376 (1925).
[2] J. Am. Chem. Soc., **48**, 236 (1926).

In the following experiments 0.415 N solution of sodium phosphate was used:

2	36.5	10	10	0.1000	0.0987	0.0013	1.3
3	36.5	20	10	0.1000	0.0916	0.0084	8.4
4	73	25	10	0.1000	0.0761	0.0239	23.9
5	36.5	25	30	0.1000	0.0678	0.0322	32.2

In the following experiments no insulin was used:

No. of experiment	Litres of air passed	Sodium phosphate (0.348N) in cc.	Actual weight of glucose in 10 cc. of the soln. taken in grm. (Blank)	Amount of glucose left after experiment in grm.	Amount of glucose oxidised in grm.	Percentage amount of glucose oxidised
1	36.5	10	0.1000	0.0997	0.0003	0.3

In the following experiments 0.415 N disodium hydrogen phosphate was used:

| 2 | 73 | 10 | 0.1000 | 0.0844 | 0.0156 | 15.6 |
| 3 | 36.5 | 30 | 0.1000 | 0.0961 | 0.0039 | 3.9 |

The above tables clearly show that there is more oxidation of glucose in presence of insulin and phosphate than in phosphate alone. This leaves no doubt that insulin acts as an inductor in the oxidation of glucose in presence of sodium phosphate. It is well known that the part which phosphate plays in the animal metabolism is unique.

We have carried on experiments with freshly precipitated cerous and ferrous hydroxides also and the results obtained conclusively prove that they also help insulin in the oxidation of glucose.

The same amount of cerous hydroxide was used in each of these experiments:

No. of experiment	Litres of air passed	Insulin in cc.	Actual weight of glucose in 10 cc. of the solution taken in grm. (Blank)	Amount of glucose left after experiment in grm.	Amount of glucose oxidised in grm.	Percentage amount of glucose oxidised
1	36.5	10	0.1000	0.0830	0.0170	17.0
2	36.5	20	0.1000	0.0789	0.0211	21.1
3	36.5	25	0.1000	0.0789	0.0212	21.2
4	73	25	0.1000	0.0675	0.0325	32.5

In the following experiments also the same amount of cerous hydroxide but no insulin was used:

| 1 | 36.5 | — | 0.1000 | 0.0845 | 0.0155 | 15.5 |
| 2 | 73 | — | 0.1000 | 0.0701 | 0.0299 | 29.9 |

In the following experiments ferrous hydroxide was used instead of cerous hydroxide:

No. of experiment	Litres of air passed	Insulin in cc.	Actual weight of glucose in 10 cc. of the solution taken in grm. (Blank)	Amount of glucose left after experiment in grm.	Amount of glucose oxidised in grm.	Percentage amount of glucose oxidised
1	73	25	0.1000	0.0806	0.0194	19.4
2	73	No Insulin	0.1000	0.0923	0.0077	7.7

We have also carried on some experiments with glucose and insulin alone and we find that there is very slight oxidation. The following results were obtained:

1	36.5	10	0.1000	0.0992	0.0008	0.8
2	36.5	25	0.1000	0.0990	0.0010	1.0

By these results we are led to believe that there is some oxidation of glucose in presence of insulin alone *in vitro*, but by adding cerous or ferrous hydroxides, which act as surfaces the oxidation is facilitated.

We have observed that insulin by itself is oxidized by passing air at 25° and carbon dioxide is evolved, but when glucose is added the oxidation of insulin is greatly retarded. This led us to believe that insulin acts as an inductor in the oxidation of carbohydrates. In several publications[1] we have shown that the slow oxidation of substances can be retarded by another reducing agent, which is slowly oxidized along with the primary reaction. The oxidation of insulin induces the oxidation of glucose.

We have tried the oxidation of glucose in presence of insulin and sodium bi-carbonate and sodium carbonate, but in the case of sodium bicarbonate we find that the oxidation is practically the same in presence or absence of insulin. In the case of sodium carbonate the results are curious. There is more oxidation in presence of sodium carbonate alone than in presence of sodium carbonate and insulin. We have obtained the following results. In the following experiments 10 cc of 1.005 N sodium bicarbonate solution was used:

No. of experiment	Litres of air passed	Insulin in cc.	Actual weight of glucose in 10 cc. of the solution taken in grm. (Blank)	Amount of glucose left after experiment in grm.	Amount of glucose oxidised in grm.	Percentage amount of glucose oxidised
1	36.5	10	0.1000	0.0983	0.0017	1.7
2	73	25	0.1000	0.0987	0.0013	1.3
3	73	No Insulin	0.1000	0.0982	0.0018	1.8

In the following experiments 30 cc. of the normal sodium carbonate solution was used:

1	36.5	25	0.1000	0.0786	0.0214	21.6
2	36.5	50	0.1000	0.0858	0.0142	14.2
3	36.5	No Insulin	0.1000	0.0703	0.0297	29.2

[1] Dhar: Proc. Akad. Wet. Amsterdam, 29, 1023 (1921); Z. anorg. allgem. Chem., 144, 289 (1925).

It is difficult to explain satisfactorily these results.

Since 1922 much experimental investigation has been carried on with insulin and its influence on glucose metabolism in the animal body and it is generally believed that it helps glucose metabolism. From our experiments it is clear that insulin plays an important part in the carbohydrates metabolism *in vitro* and it acts as an inductor. It is easily oxidised by passing air and when mixed with glucose solution the oxidation of insulin is retarded, while it helps the oxidation of glucose. On addition of sodium phosphate or cerous or ferrous hydroxide the oxidation of insulin is accelerated and there is a large amount of carbon dioxide liberated and at the same time the oxidation of glucose is also increased. Sodium phosphate and cerous and ferrous hydroxides facilitate the oxidation of glucose. In the animal body also phosphate is present which must be helping the oxidation of glucose by the secretion of the pancreas. Moreover, surfaces are also present in the animal system.

The behaviour of insulin resembles that of glutathione. Glutathione is an auto-oxidisable substance. It oxidises itself by the oxygen of the atmosphere and at the same time induces the oxidation of the cell constituents. Harrison[1] has shown that traces of iron cause a marked acceleration in the auto-oxidation of glutathione; and hence the oxidation of tissue components induced by glutathione will also be accelerated by iron. The same behaviour is seen in the case of insulin also and our experiments show that insulin, like glutathione is our auto-oxidisable substance, which induces the oxidation of glucose in the animal system.

It is probable that insulin is a polypeptid, a group of substances known to participate in important ways in the metabolism of the body. When analysed by the method of Folin and Looney, there is found 17.9% tyrosin, 7.1% cystin, 0.8% tryptophan and 8.5% histidin in insulin. Insulin is not digested by pepsin nor by trypsin, but in an alkaline medium, in which trypsin is present, insulin becomes inactivated. It may be reactivated, however, showing that it is not destroyed. It appears from our experimental results that in presence of sodium carbonate, insulin is inactivated and does not increase the oxidation of glucose by air *in vitro*.

It will be interesting to note here that Bertrand and Mâcheboeuf[2] have found that insulin contains very small amounts of nickel and cobalt salts (the amount is never greater than a fraction of a milligram per kilo of tissue). The amount of sugar metabolised under the action of insulin is increased when nickel or cobalt compound is given simultaneously.

The recent results obtained by Svedberg[3] seem to demonstrate that insulin is a well-defined protein belonging to the same class as egg albumin and Bence Jones protein. As pointed out by Dr. H. Jensen of the Johns Hopkins University, Baltimore, this fact makes it very improbable that the synthesis of insulin will ever become possible.

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[1] Biochem. J., 18, 1009 (1924).

[2] Compt. rend., 182, 1305, 1506; 183, 5, 257, 326 (1926).

[3] Nature, 127, 438 (1931).

Summary

(1)   Glucose is appreciably oxidised by passing air through solutions of glucose in presence of insulin at $25°$.   Phosphates, cerous and ferrous hydro-oxides markedly accelerate this induced oxidation of glucose by air in presence of insulin.

(2)   Insulin is oxidised by passing air and in presence of glucose, the oxidation of insulin is retarded but the oxidation of insulin induces the oxidation of glucose.   This is the probable mechanism of the increased oxidation of glucose in presence of insulin in the animal body.

(3)   Sodium carbonate appears to inactivate insulin and in presence of sodium carbonate, there is no increase in the oxidation of glucose due to insulin.

Chemical Laboratory,
Allahabad University,
Allahabad, India,
May 24, 1931.

THE APPLICATION OF THE MUDD INTERFACIAL TECHNIQUE IN THE STUDY OF PROTECTIVE PROTEIN FILMS IN OIL-IN-WATER EMULSIONS

BY ROBERT LOGAN NUGENT

Introduction

At the present time it is quite generally agreed that the emulsifying agent in an-oil-in-water emulsion acts by being adsorbed in the oil-water interface. In this way protective films are formed around the oil droplets which prevent their coalescence, and thus stabilize the emulsion. Clayton refers to this general view as the modern adsorption film theory of emulsion stability.[1] In its present form it is due to Bancroft[2] who first stated the underlying principles in 1913.

In the past the investigation of the relative efficiencies of different emulsifying agents, or of the same emulsifying agent under different conditions, has been almost entirely on the basis of the observation of the relative ease of emulsification or of the relative stability of the formed emulsion under the different conditions.[3] In practical work experiments of this type furnish the proof of the pudding. However, on the basis of the modern theory, one would expect that information of both practical and theoretical value might be obtained from a study of the properties of protective films on single emulsion droplets. In this latter connection microcataphoresis has indeed afforded a convenient means of investigating the electrokinetic properties of single oil-in-water droplets. The outstanding result from such experiments is that protected droplets exhibit, in general, the electrokinetic properties of the protective agent. Thus paraffin oil droplets emulsified with gelatin are isoelectric at the isoelectric point of gelatin, pH 4.7.[4] When treated with blood serum, they assume an isoelectric point characteristic of the serum proteins, pH 4.7-4.8.[5] Free fat is transported by the blood as an emulsion of fine droplets called chylomicrons.[6] The chylomicrons also exhibit an isoelectric point characteristic of the serum proteins, pH 4.8-5.0, indicating that they are surrounded by films of serum protein.[7]

Cataphoresis experiments have thus afforded quantitative evidence of the correctness of the modern theory. In so far as the droplets in the cases

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[1] Clayton: "The Theory of Emulsions and Their Technical Treatment," 120 (1928).

[2] Bancroft: J. Phys. Chem., 17, 415 (1913); 19, 275 (1915).

[3] See Clayton: loc. cit., Chapters IV, VI, and VIII; Fischer and Hooker: "Fats and Fatty Degeneration" (1917); Holmes and Child: J. Am. Chem. Soc., 42, 2049 (1920); Krantz and Gordon: Colloid Symposium Monograph, 6, 173 (1928).

[4] Limburg: Rec. Trav. chim., 45, 885 (1926).

[5] Abramson: J. Gen. Physiol., 13, 177 (1929).

[6] Ludlum, Taft and Nugent: Colloid Symposium Annual, 7, 233 (1929).

[7] Ludlum, Taft and Nugent: Proc. Soc. Exptl. Biol. and Med., 28, 189 (1930); J. Phys. Chem., 35, 269 (1931).

referred to, are surrounded by protective films of protein, they should exhibit
the electrokinetic properties of protein, as has been found to be the case.
Microcataphoresis thus affords a means of studying the "charge" on oil in
water emulsion droplets. It is inadequate in any complete study of the pro-
tective properties of films on single droplets, because, as is well known,
"charge" alone is inadequate in stabilizing dispersions of oil in water except
in the case of extremely dilute dispersions of purely theoretical importance.[8]

The interfacial technique of Mudd and Mudd[9] seemed to offer a valuable
method for the study of other properties of protective films on single oil-in-
water emulsion droplets, such as their state of hydration and their resistance
to disruption under the action of interfacial and mechanical forces. The
present paper demonstrates that such is actually the case on the basis of
experiments with droplets with protective films of protein. Proteins were
chosen as the emulsifying agents for these first studies, because they are
typical of the general class[10] and because results obtained with them might
be more directly applicable in the explanation of biological surface phenomena
than similar results with other typical agents such as soaps and gums. The
first objective was the examination and description of the behavior of such
droplets under various conditions, and the second the interpretation of the
observed types of behavior and the support of this interpretation by means of
independent evidence. These objectives have been accomplished, and lead
the way to the use of the interfacial technique in the study of emulsions and
protective action. A striking fact is that a simple comparison of the behavior
of protected and unprotected droplets leads immediately to a novel visual
demonstration of the correctness of the modern adsorption film theory.

If the stability of various oil-in-water emulsions is determined largely by
the properties of the protective films in the several cases, it should be possible
to predict relative emulsion stabilities from a study of the properties of the films
on single droplets. Experiments are described which demonstrate that it is
actually possible to predict the relative stabilities of a series of emulsions in
this way. This fact, in itself, affords interesting independent evidence of the
correctness of the adsorption film theory. It further opens the way to the use
of the interfacial method in the practical study of the stability of oil-in-water
emulsions.

As has been mentioned, oil droplets protected by means of protein films
exhibit, in general, the electrokinetic properties of the protein. It is of
interest from the point of view of the theory of surface films and protective
action to know whether the condition of hydration of protective protein films
also varies with conditions in the same manner as does that of particles of the
same protein in solution. Loeb has shown by means of indirect experimental
evidence that it does in the case of gelatin films on collodion particles and does
not in the case of albumin films on collodion particles.[11] The question is to

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[8] See Kruyt translated by van Klooster: "Colloids," 243 (1927).

[9] Mudd and Mudd: J. Expt. Med., **40**, 633, 647 (1924).

[10] Gortner: "Outlines of Biochemistry," 34 (1929).

[11] Loeb: "Proteins and the Theory of Colloidal Behavior," 349 (1924).

obtain direct experimental evidence 'n any given system. The interfacial technique is shown to afford a means of obtaining such evidence. The experiments indicate that, in the single case investigated, the condition of hydration of the protective protein films actually does vary in the same manner as does that of particles of the same protein in solution.

According to Bancroft, any substance will act as a protective agent if it is adsorbed in the interface and forms there a sufficiently viscous or plastic film.[12] Actually it is well known that most practically important oil-in-water emulsions are stabilized by means of substances such as proteins, soaps and gums which form colloidal solutions in water in which the dispersed particles are of a hydrous nature.[13] It is highly probable that such substances have the property of forming films of the proper viscosity or plasticity. It is also highly probable that their state of hydration is an important factor *per se*.[14] Kruyt has clearly pointed out the independent importance of hydration in determining the stability of colloidal solutions of these typical protective agents.[15] The hydration of particles dispersed in water tends to prevent their aggregation. Similarly the hydration of protective films would tend to prevent the aggregation of emulsion droplets which, presumably, must be the first stage in any coalescing process. The rôle of film hydration *per se* is quite clear on this basis.

It has been mentioned that the interfacial technique affords a means of studying the relative states of hydration of protective protein films. It also affords a means of examining their resistance to disruption under the action of interfacial tension and simple mechanical forces. It thus affords, in addition, a means of experimental differentiation between two important protective properties of films, their resistance to disruption as determined by their viscosity or plasticity and their state of hydration *per se*. An example of such differentiation is described.

The Mudd Interfacial Technique

The interfacial technique of Mudd and Mudd has been used most successfully by them and by others in the study of biological surfaces.[16] In its use a drop of a suitable oil and a drop of an aqueous suspension of the particles to be studied, bacteria, blood cells, protein particles, etc., are placed upon a microscope slide with relative positions and sizes as shown diagrammatically in Fig. 1 I. A rectangular coverslip is then held with forceps, and allowed to make contact with the oil drop as shown in Fig. 1 II, and is then gently lowered into position over both the oil and aqueous drops. Under these conditions they spread under the coverslip with the formation of an oil-water

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[12] Bancroft: "Applied Colloid Chemistry," Chapter XII (1926).

[13] Bancroft: loc. cit., page 355; Gortner: loc. cit., page 34.

[14] Compare Gortner: loc. cit., page 42.

[15] Kruyt translated by van Klooster: loc. cit., page 180; Kruyt and Bungenberg de Jong: Z. physik. Chem., **100**, 250 (1922).

[16] E.g. Mudd and Mudd: J. Exptl. Med., **40**, 633, 647 (1924); **43**, 127 (1926); **46**, 167, 173 (1927); Mudd, Lucké, McCutcheon and Strumia: Colloid Symposium Monograph, **6**, 131 (1928); Mudd and Mudd: J. Gen. Physiol., **14**, 733 (1930-31).

interface as shown diagrammatically in Fig. 1 III. The oil gradually displaces the water with the result that the interface moves slowly to the water side, in the direction of the arrow in Fig. 1 III. The moving interface is followed microscopically using a mechanical stage, any desired combination of ocular and objective and either dark- or light-field illumination. Ordinarily dark-field illumination is more convenient.
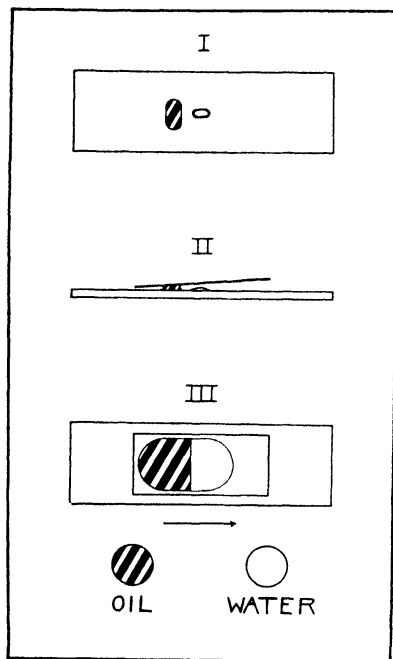
FIG. 1

Drawings to illustrate the relative sizes of the oil and aqueous drops, the application of the coverslip and the formation of the interface in the Mudd interfacial technique.

The moving interface is seen gradually to overtake the suspended particles or aggregations of particles.[17] In general, observation is made of the behavior of these when thus subjected to the action of the interfacial forces. When the particles or aggregates adhere to the slide or coverslip, it is possible to observe the resistance which they offer to wetting by the oil, and in some cases, the effect upon them due to mechanical stretching and compressing forces. It is essential that the slide and coverslip be thoroughly clean in all cases.

Particles with oil-like (lipoid) surfaces pass easily and directly into the advancing oil phase. Particles with strongly hydrous surfaces show the extreme type of resistance to passage into the oil. The advancing oil film flows around such particles finally uniting on the far side leaving them in the oil phase still surrounded by a drop of water.[18]

The descriptions of the previous paragraph apply particularly to particles or aggregates of particles which are more or less firmly fixed to the slide or coverslip. When freely floating in the aqueous phase, particles with markedly oil-like surfaces pass spontaneously into the oil. Those with markedly hydrous surfaces remain in the aqueous phase and are pushed ahead by the advancing interface, and those with intermediate types of surface are observed to concentrate preferentially in the interface itself. Those three types of action are in accord with experimental behavior observed when the three types of particles are shaken with oil and water. Those more readily wetted by oil concentrate in the oil and those more readily wetted by water concentrate in the water phase. Those wetted readily by both oil and water tend to concentrate in the interface.[19] Mudd and Mudd have analyzed the three

[17] Mudd and Mudd: J. Exptl. Med., 40, 633 (1924).

[18] Compare Mudd and Mudd: J. Exptl. Med., 40, 633 (1924).

[19] See Bancroft: "Applied Colloid Chemistry," 100 (1926); Reed and Rice: J. Bacteriol., 22, 239 (1931).

types of behavior on the basis of surface tension relationships.[20] Aggregates of particles are frequently seen to be disrupted by the interfacial forces. Under these conditions, the constituent particles are sometimes scattered in the oil phase and sometimes spread along the interface.[21]

In using the interfacial technique, one is thus able actually to observe the processes of preferential wetting, interfacial adsorption and the dispersion of aggregates taking place before one's eyes.[22] The technique is directly applicable to the study of aqueous suspensions of oil droplets, that is to the study of oil-in-water emulsions. In this connection the experimental material of the present paper demonstrates that one is also actually able to observe the protective action of films of emulsifying agent, the relative states of hydration of such films and their destruction or resistance to destruction under the action of interfacial and mechanical forces. It is possible to observe the actual stretching of protective films. Such stretching may or may not be followed by disruption.

Methods and Materials

The experiments described have all been done with droplets from two "stock" emulsions, fifty percent by volume of commercial "Pompeian" olive oil emulsified in one percent solutions of Eastman Kodak Co.'s ash-free gelatin, as a representative synthetic emulsion, and cream from raw sweet milk as a representative natural emulsion. In the first case twenty-five cc. each of the olive oil and the gelatin solution were added to a 150 cc. Florence flask and given nine fifteen-second shaking-periods by hand (about forty-five double shakes each) with thirty second rest intervals between shakings. The method is similar to one which has been used by Seifriz[23] and takes advantage of the intermittent shaking principle of Briggs.[24] It is important to use this method of preparation in any attempt to repeat the results to be described. It has been shown that ease of emulsification and the stability of formed emulsions depend upon the speed and mode of agitation and the dimensions of the vessel employed in the emulsification process.[25] Oil-in-water emulsions result with droplets varying from about one to fifty microns in diameter.

Milk and cream are emulsions of butter fat in milk plasma,[26] in which the droplets are of the order of six microns in diameter.[27] There is considerable question at present as to whether or not the protective agent is ordinary casein or whether a special protein is the important substance.[28] For the present purpose, it is sufficient that cream is an oil-in-water emulsion in which the oil droplets are protected by films of a protein nature.[29]

[20] Mudd and Mudd: J. Exptl. Med., 40, 647 (1924).
[21] Mudd and Mudd: J. Exptl. Med., 40, 633 (1924).
[22] See Seifriz in Alexander: "Colloid Chemistry," 2, 437 (1928).
[23] Seifriz: Am. J. Physiol., 66, 124 (1923).
[24] Briggs: J. Phys. Chem., 24, 120 (1920).
[25] Briggs and Schmidt: J. Phys. Chem., 19, 478 (1915).
[26] Heineman: "Milk," 51 (1919).
[27] Heineman: loc. cit., page 56.
[28] See for example Titus, Sommer and Hart: J. Biol. Chem., 76, 237 (1928).
[29] Gortner: loc. cit., page 34.

In all the experiments the aqueous drop, containing the emulsion droplets to be examined by the interfacial method, was taken from a dilute emulsion containing one or two drops of one of the two stock emulsions in ten cc. of either a buffer solution or of a hydrochloric acid solution. There are three reasons for the use of this dilution procedure. First, it is necessary in order to avoid overcrowding the interface with droplets and thus to enable the observer to concentrate upon the behavior of single droplets. Secondly the concentration of emulsifying agent is one hundred to two hundred times lower in the diluted emulsions. The tendency for protein to concentrate in the advancing oil-water interface is lessened by the dilution, and one is therefore able to observe the behavior of the droplets at an interface which is not clogged with protein. Experience has shown that good results are not obtained when the aqueous drop contains high concentration of protein.

The experiments with droplets from both of the stock emulsions involved the observation of their interfacial behavior at a series of pH values. It is apparent that, if a drop of one of the stock emulsions is added to ten cc. of a pH 7.4 buffer solution, a dilute emulsion is obtained in which the protective protein films assume properties characteristic of that pH value, assuming that the dilution is not so great that sufficient protein to form continuous films is no longer retained on the surface of the droplets. Similarly by adding drops of the stock emulsions to a series of buffer solutions and then using drops of the resulting dilute emulsions for the interfacial procedure, it is possible to examine the behavior of droplets surrounded by films of the particular protein at a series of pH values. One stock emulsion suffices in each case, doing away in the case of synthetic emulsions, with the necessity of making up a series of original emulsions, and in the case of cream, with the necessity of adjusting cream samples to the several pH values. This convenience constitutes the third reason for using the dilution procedure.

There are two apparent possible objections to the dilution procedure just described. The first has been suggested as that, in the diluted emulsions, sufficient protein to form continuous films around the droplets might no longer be retained upon their surfaces. A criterion which has been used for the presence of complete films in cases of this sort is that the droplets show the isoelectric point of the film substance.[30] Cataphoresis experiments were accordingly performed to test this point in the cases of the dilute emulsions described.

A series of dilute emulsions in 0.1 molal buffer solutions was prepared from each of the two stock emulsions and also from an emulsion of olive oil with Merck's powdered egg albumin as the emulsifying agent, prepared in exactly the same way as described for the olive oil emulsion with gelatin as the emulsifying agent. The relative cataphoretic velocities of the droplets in each dilute emulsion were observed using a Northrop-Kunitz microcataphoresis

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[30] See Limburg: loc. cit.; Abramson: Colloid Symposium Monograph, **6**, 128 (1928).

cell[31] with accessory apparatus arranged according to Mudd.[32]   On the alkaline side of the isoelectric point of their surface films, emulsion droplets migrate to the anode and on the acid side to the cathode.   Theoretically the migration velocity is zero at the isoelectric point.   Plotting relative cataphoretic velocities against pH values, one obtains the pH of the isoelectric point by noting the pH value corresponding to zero migration velocity.[33] Fig. 2 shows the results obtained in each of the three series of dilute emulsions.   The isoelectric point of the olive oil droplets emulsified with gelatin is indicated to be at pH 4.7, that of the olive oil droplets emulsified with
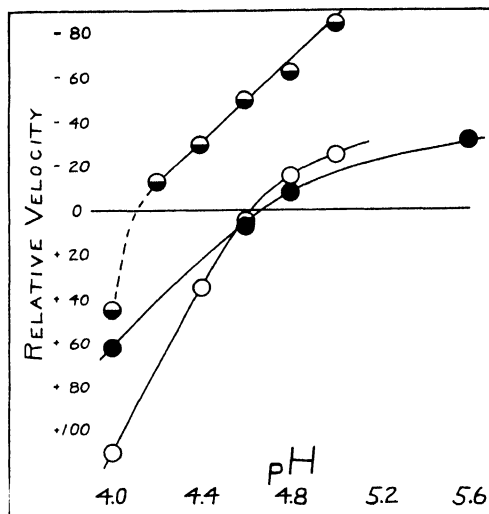
FIG. 2

Data showing the isoelectric points of olive oil droplets emulsified respectively with gelatin (solid dots) and egg albumin (circles) and of fat droplets from cream (divided circles). In the same order the indicated isoelectric points are at pH 4.7, pH 4.6 and pH 4.1.

egg albumin to be at pH 4.6 and that of the milk fat droplets at pH 4.1. The first two agree with the accepted isoelectric points of the two proteins at least to within 0.2 pH[34] which is within the limits of accuracy of the method when so few points are determined.   The indicated isoelectric point of the milk fat droplets is close to a value obtained by others.[35]

   The cataphoresis experiments thus indicate that in the dilute emulsions continuous films of protein are still present around the droplets.   This conclusion is in agreement with the results of Limburg[36] who found that, in the

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   [31] Northrop and Kunitz: J. Gen. Physiol., 7, 729 (1924-25); See also Mudd, Lucké, McCutcheon and Strumia: loc. cit., footnote page 134.
   [32] The cell with accessory apparatus may be purchased from the Arthur H. Thomas Co., Philadelphia.
   [33] See for example Abramson: J. Gen. Physiol., 13, 177 (1929).
   [34] Michaelis and Grineff: Biochem. Z., 41, 373 (1912); Loeb: J. Gen. Physiol., 1, 241 (1918-19); Hitchcock: J. Gen. Physiol., 14, 685 (1930-31); Sörensen: Compt. Rend. Trav. Lab. Carlsberg, 12, 149 (1915-17); See Mudd: J. Gen. Physiol., 7, 389 (1924-25) for a table of isoelectric points.
   [35] Personal communication from Dr. R. A. Gortner.
   [36] Limburg: loc. cit.

isoelectric region, less than 0.0002 percent of gelatin need be present in the water phase in order to give dispersed paraffin oil droplets an isoelectric point at pH 4.7. In the dilute emulsions described here, the concentrations of protein were at least fifty times greater than this value.

The second possible objection to the dilution procedure would be that, even though continuous films of protein were present around the droplets in the dilute emulsions, these films might have different protective properties from those in the concentrated protein solution in the original emulsion. Such may well be the case. However the discussion in the present paper applies throughout to relative differences in interfacial behavior as indicating relative differences in film properties under various conditions. Thus as long as the same dilution prevails throughout a series of experiments, one observes the relative behavior of films of the particular protein under the several conditions. Theoretically the presence of a continuous protein film is the only necessary condition for the suitability of the dilution procedure employed. This condition is met as shown by the cataphoresis experiments described.

In using the interfacial technique, it is important to compare the behavior of particles or aggregates of closely the same size with closely the same speeds of advance of the interface and thicknesses of the oil film. The latter two conditions are usually met by using the same sizes of oil and aqueous drops in all cases and applying the coverslip in the same manner. In the present work, the results all refer to the behavior of droplets from eight to fourteen microns in diameter with speeds of interfacial advance varying from three to eight microns per second. The measurements are made with an ocular micrometer calibrated against a stage micrometer.

Kahlbaum's triolein was used as an interfacial oil in all the experiments. In certain cases comparative observations were made using a mineral oil, commercial "Nujol." It is absolutely essential to use these oils in any attempt to repeat the results reported. Mudd and Mudd have described the use of a large number of interfacial oils and have shown that the results obtained vary markedly with the oil employed. An 8 mm. objective was used throughout as was the ocular micrometer mentioned above. Dark- and light-field illumination were used interchangeably. The former is usually much more convenient and was obtained using a Zeiss cardioid condenser. The beginner may well be confused by the behavior of air bubbles in the preparation. Using light-field illumination, a simple test described by Chamot and Mason[37] serves readily to distinguish between oil droplets and air bubbles.

General Types of Behavior observed

The first objectives of the work were the examination and description of the behavior of the emulsion droplets when examined by means of the interfacial technique and the interpretation of the observed phenomena together with the attainment of independent evidence in support of the interpretation based on appearance alone. This section of the paper presents

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[37] Chamot and Mason: "Handbook of Chemical Microscopy," 1, 368 (1930).

the general types of behavior observed with the interpretation of each based on appearance alone. In the following sections the experimental results are referred to the types of behavior described here. Such independent evidence as was obtained for each interpretation is also discussed in the following sections.
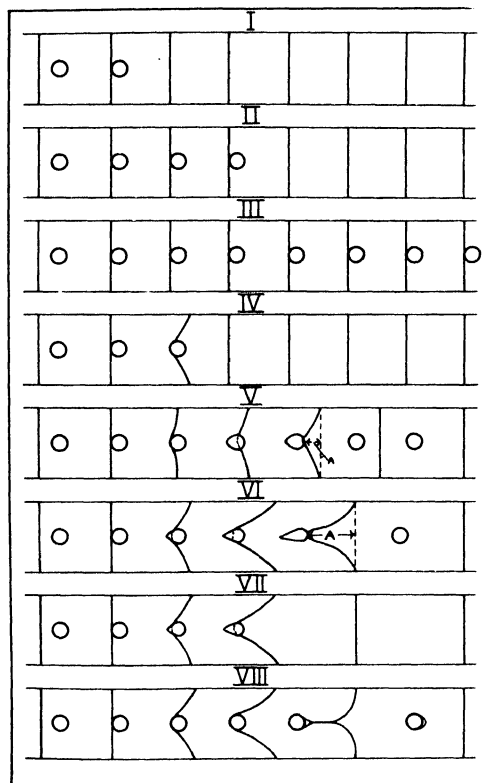
Fig. 3

General types of behavior observed in the study of oil droplets with protective protein films by means of the Mudd interfacial technique.

Fig. 3 illustrates the eight general types of behavior observed. The eight vertical lines in Figs. 3 I–3 IV and the corresponding lines in Figs. 3 V–3 VIII represent successive positions of an advancing interface in relation to an oil droplet. The first position in each case represents the interface approaching the droplet and the second position the instant of contact of the interface with the droplet.

Fig. 3 I.—On contact with the interface the film, if any, around the droplet is either immediately disrupted or disrupted after an extremely slight pause in the advance of the interface. The oil of the droplet is simultaneously dissolved in the oil of the advancing film with the result that in such cases, the droplet seems to disappear almost instantaneously on contact with the interface. Such a disappearance of a droplet will hereinafter be referred to

as the "explosion" of the droplet. Unprotected oil droplets show this general type of behavior as do droplets with films of the lowest grade of protective power. The interpretation in the latter case is that the film around the droplet is practically immediately disrupted by the interfacial forces. It indicates low film resistance and comparatively low film hydration.

Fig. 3 II.—Droplets sometimes remain in contact with the interface for varying short lengths of time and then "explode." Sometimes the interface merely seems to pause for a fraction of a second on contact with the droplet before "explosion" occurs. Droplets which do not adhere strongly to the slide or coverslip may be simply pushed ahead by the interface for varying lengths of time before "explosion" occurs. The average length of time of carry as measured with a stop-watch or a metronome seems to be a fair measure of resistance to disruption in a series of preparations showing this general type of behavior. The interpretation is that either the resistance of the film to disruption or the film hydration or both are sufficiently greater than in the case shown in Fig. 3 I better to protect the film from the disrupting action of the interfacial forces. Any comparison of results such as Fig. 3 I and Fig. 3 II implies that conditions at the advancing interface remain the same.

Fig. 3 III.—This type of action is simply the extreme case of the type illustrated in Fig. 3 II. The droplets are permanently pushed ahead by the interface without disruption of the protective films. It is apparent that this is the maximum observable type of protective action in the case of films on freely floating droplets. This type of action must be due to comparatively strong resistance to disruption, to considerable film hydration or to both. Types 3 I, 3 II and 3 III distinguish weak protective action from strong protective action, but do not clearly distinguish between the resistance of the films to disruption due to interfacial or mechanical forces and protection due to the hydration of the films *per se*.

Fig. 3 IV.—Here one is dealing with a droplet which is more or less firmly attached to the slide or coverslip. The interface undergoes slight local retardation after making contact with the droplet, and the droplet then "explodes." This indicates low film strength. The film either disrupts under the action of the interfacial forces or under some slight compressing or stretching force due to the resistance of the droplet to being pushed ahead by the interface.

Fig. 3 V.—Here as in Fig. 3 IV one is dealing with a droplet which adheres more or less firmly to the slide or coverslip. The interface flows readily over the droplet *leaving it intact in the oil phase*. The interface suffers only slight local retardation in the process. The fact that the film is not disrupted by the interfacial forces indicates a considerable resistance to such action. The slight local retardation in passing over the droplet indicates a low order of hydration of the droplet surface, that is to say a relatively great ease of wetting of the surface of the droplet by the oil. There is very little visible deformation of the droplet during the process upon which to base an opinion as to the ability of the film to resist stretching and compressing forces.

Fig. 3 VI.—The local retardation of the interface may be slight as in Fig. 3 V, indicating low film hydration and relative ease of wetting by the oil, or it may be increasingly greater indicating increasing hydration of the droplet surface and greater difficulty of wetting by the oil as shown in Fig. 3 VI. Using the micrometer ocular it is quite easy to measure the retardation of the interface at the moment it finally breaks away leaving the droplet intact in the oil. This distance is shown as "A" in Figs. 3 V and 3 VI. Expressed in microns it is apparently a fair measure of relative degrees of film hydration in a series of cases.

Here as in Fig. 3 V the non-disruption of the film under the action of the interfacial forces indicates definite resistance to disruption. In this type however, evidence is also afforded as to the ability of the film to resist disruption due to stretching. The droplet is stretched into a pear shape with the stem at the point of attachment to the glass, going back to its original spherical shape after passing intact into the oil phase. Oil droplets intact in an oil phase may be said to constitute an "oil-in-oil" emulsion system.

Fig. 3 VII.—This type is exactly like that illustrated in Fig. 3 VI except that the droplet "explodes" when stretched into the pear shape, indicating less resistance to stretching than in that case. Considerable hydration and the ability to resist disruption due to the interfacial forces is indicated as in type Fig. 3 VI.

Fig. 3 VIII.—In this type of action the film hydration is apparently so great that the advancing oil is unable to flow over the droplet and flows around it, finally uniting on the far side leaving the droplet in the oil phase still surrounded by a drop of aqueous phase. The indication is of the greatest observable type of hydration and possibly of marked resistance to disruption under the action of the interfacial forces.

The Interfacial Behavior at Different pH Values of Olive Oil Droplets emulsified with Gelatin

As described under Methods and Materials, two drops of the stock emulsion of olive oil in one percent gelatin solution were added to ten cc. each of a series of 0.1 molal acetate and phosphate buffer solutions ranging from pH 3.6 to pH 7.4 in this case. The addition of one-hour-old stock emulsion was made to each of the buffer solutions at the same time. The behavior of several hundred droplets from at least ten different stock emulsions has been observed for each pH value. Triolein was used as the interfacial oil throughout.

At all pH values within this range, the droplets show a marked tendency to adhere to the slide or coverslip. Further they show considerable film strength, and tend to pass intact into the oil phase after causing varying degree of retardation of the interface. (Figs. 3 V and 3 VI). It has been remarked that when a droplet causes more or less retardation of the interface and then passes intact into the oil phase, the retardation in microns at the moment the interface finally breaks away from the droplet would seem to

be a fair measure of the relative degrees of film hydration in a series of cases. It is apparent that the results with olive oil droplets with gelatin films may be conveniently treated in this way. Fig. 4 shows the results for a series from one stock emulsion. The average retardations for all droplets observed at each pH value are plotted against the corresponding pH values. The minimum retardation close to the isoelectric point was observed in each of ten experiments with series from different stock emulsions. In most cases the minimum was not so sharp as in the case illustrated in Fig. 4.
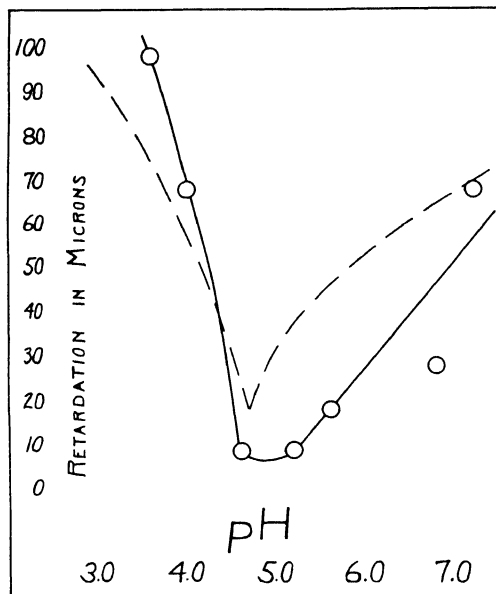
FIG. 4

Variation with pH of the ease with which an advancing triolein film passes over olive oil droplets protected with gelatin films. The smaller the retardation in microns, the greater the ease of wetting. The dotted curve illustrates the manner of variation of the viscosity of a gelatin solution over the same pH range.

It is generally believed that the hydration of gelatin particles in solution exhibits a minimum at the isoelectric point of gelatin.[38] The relative viscosities of gelatin solutions at different pH values are presumably measures of the relative states of hydration of the gelatin particles under the several conditions.[39] The dotted curve in Fig. 4 shows the variation of the viscosity of a gelatin solution with pH over the range pH 3.6 to pH 7.4.[40]

It is quite reasonable to interpret increasing degrees of interface retardation as due to increasing degrees of hydration of the droplet surfaces. The more hydrous the surface, the less readily it would be wet by the advancing oil. The less readily wet by the oil, the more difficult would be the passage

[38] See Kruyt translated by van Klooster: loc. cit., page 197.
[39] See Kruyt translated by van Klooster: loc. cit., Chapter XII.
[40] See Kruyt translated by van Klooster: loc. cit., page 196.

of the oil over the droplet and consequently the greater the local retardation of the interface. Fig. 4 indicates that the relative degrees of retardation actually follow the relative degrees of hydration of gelatin particles in solution under the same pH conditions. This fact affords independent evidence of the correctness of the interpretation based upon appearance alone. In addition, so far as known to the writer, Fig. 4 illustrates the first direct experimental evidence that the state of hydration of protective protein film may vary in the same manner with conditions as does that of particles of the same protein in solution.

Close to the isoelectric point (pH 4.7) the behavior is like that illustrated in Fig. 3 V. Near pH 2.0 is the best region to observe behavior like that illustrated in Fig. 3 VI. Both types indicate strong resistance to disruption by the interfacial forces and resistance to disruption due to mechanical stretching. At pH values above 6.0, complete hydration resistance is frequently observed (Fig. 3 VIII). In this region also many of the droplets are of the free floating type, and these always exhibit permanent carry by the interface as illustrated in Fig. 3 III. Complete hydration resistance was also observed in some cases in the region pH 2.0-pH 3.6. These facts emphasize the hydrous nature of the films under these conditions as compared with their condition close to their isoelectric point.

In a large number of cases droplets in the region near pH 2.0 showed definitely greater local retardation of the interface than in the isoelectric region, but exploded as in Fig. 3 IV. This example demonstrates the fact that the interfacial method is capable of differentiating the important protective factors, resistance to disruption and hydration *per se*.

In interpreting the behavior at different pH values as has been attempted above, possible variations in the conditions at the advancing oil-water interface must be considered. Donnan found that a pure mineral oil had closely the same surface tension against 0.01 N sodium hydroxide as against water, as did a purified neutral olive oil.[41] However the surface tension of commercial olive oil was much lower against the dilute hydroxide, presumably due to its fatty acid content leading to soap formation at the interface. Mineral oil containing 0.6 percent commercial stearic acid had a much lower surface tension against 0.001 N sodium hydroxide than against water. Hartridge and Peters later determined the interfacial tensions of purified olive oil against a series of buffer solutions.[42] In general they found a constant interfacial tension between pH 3.0 and pH 5.0 with a drop of about eleven percent between pH 5.0 and pH 5.6, and a drop of about thirty-two percent between pH 5.0 and pH 7.0. At pH values greater than 8.0 the surface tension became very low indeed, presumably due to the formation of soap at the interface.

On the basis of the foregoing results, the question arises as to what extent one is justified in interpreting the interfacial results of this section in terms of variation in the properties of the protective films with pH. The important observation is that of the minimum resistance to wetting by the oil close

[41] Donnan: Z. physik. Chem., **31**, 42 (1899).

[42] Hartridge and Peters: Proc. Roy. Soc., **101A**, 348 (1922).

to the isoelectric point. The results of Hartridge and Peters indicate that the increased resistance on the acid side is not due to surface tension changes at the advancing oil water interface. The increased resistance on the alkaline side between pH 4.7 and pH 5.6 is presumably accompanied by a maximum decrease in the surface tension at the advancing interface of about eleven percent. In view of the similar increase in resistance on the acid side with no variation in this surface tension, it seems probable that the increased resistance on the alkaline side between pH 4.7 and pH 5.6 is also due to a change in the protective films.

The increased resistance at pH values greater than 6.0 may well be a composite result of changes in the films and at the advancing interface as well. In this connection, the interfacial behavior of droplets at pH 4.6 has been compared with that at pH 7.4 using a mineral oil (commercial "Nujol") as the interfacial oil. A marked increased resistance to wetting by the oil was observed at the higher pH value just as in the case where triolein was used as the interfacial oil.

The Prediction of the Relative Stabilities of a Series of Emulsions

Holmes and Child have studied the relative stabilities of a great number of emulsions of kerosene in water with gelatin as the emulsifying agent.[43] In one of their series seventy-five percent by volume of kerosene was emulsified in 0.75 percent gelatin solutions containing various concentrations of salts, acids and bases. The same method of preparation was used in all cases, and the emulsions were placed aside and allowed to stand for from three to four months. Their relative stabilities were then estimated from the degree of cracking which had taken place and were classified in six groups as "none," "bad," "poor," "fair," "good," and "fine." When the 0.75 percent gelatin was made up in normal hydrochloric acid, the stability was classified as "none." With 0.5 N hydrochloric acid, it was classified as "bad"; with 0.1 N acid as "poor" and with 0.005 N acid as "good."

From the present point of view, these findings are interpreted as that the gelatin films around the kerosene droplets vary in protective power increasing in the series from normal to 0.005 normal hydrochloric acid, due to increasing resistance of the films to disruption, increasing film hydration, or to both. It is to be expected that the relative order of stability under these conditions of acidity is independent of the mechanical method employed in making the emulsions, as long as the same method is employed in making each member of a given series. The absolute variation in stability between two series in which different methods of emulsification were employed might of course be extreme. The order of relative stability in any given series should depend upon the relative protective powers of the gelatin films under the given environmental conditions.

To test this point fifty percent by volume of olive oil was emulsified in one percent gelatin solutions made up in normal, half-normal, tenth-normal and two-hundredth-normal hydrochloric acids respectively. The method in

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[43] Holmes and Child: loc. cit.

each case was the same as that described for the stock emulsion with gelatin as the emulsifying agent. The absolute stabilities of these emulsions were much lower that those of the corresponding emulsions of Holmes and Child, as would be expected from the shaking methods employed in the two cases. Further, fifty percent by volume of olive oil was used in one percent gelatin solutions rather than seventy-five percent by volume of kerosene in 0.75 percent gelatin solutions. Nevertheless the relative order of the stabilities was the same. The emulsions were placed aside and the times noted at which definite signs of cracking appeared in each case. They appeared first in the emulsion in normal acid and then in the emulsions in 0.5, 0.1 and 0.005 normal acids in order.

The next question was to examine olive oil droplets with gelatin films under these four conditions by means of the interfacial technique to see whether this same relative stability order would be predictable from the interfacial behavior. This should be possible in so far as, first, the relative stabilities depend upon the relative properties of the respective surface films and secondly, the interfacial behavior gives an interpretable picture of these properties. Accordingly two drops of a fresh stock emulsion of olive oil with gelatin as the emulsifying agent were added to ten cc. each of the four hydrochloric acids and drops of the four resulting dilute emulsions were used for the interfacial examination. Triolein was used as the interfacial oil throughout.

Droplets from the normal hydrochloric acid "exploded" immediately upon being touched by the interface. (Fig. 3 I). Those from the 0.5 N acid resisted slightly and then "exploded." (Fig. 3 IV). The droplets from the 0.1 N acid exhibited still greater local retardation before "explosion" or, in some cases passage intact into the oil. (Fig. 3 V). Finally the droplets from the 0.005 N acid exhibited the greatest local retardation before "explosion," or, in a considerable number of cases, passage intact into the oil, with definite resistance to disruption due to being stretched into the typical pear shape. (Fig. 3 VI).

The obvious interpretation of this series of experiments is that on going from gelatin films in contact with normal hydrochloric acid to those in contact with 0.005 N hydrochloric acid, there is a marked increase in the resistance of the films to disruption due to interfacial and mechanical forces. The correct relative stability order is thus predictable from the interfacial behavior in the several cases. This experiment points the way to the possibility of the use of the interfacial method in the practical study of the stability of emulsions. It is very far from establishing a practical method, since that necessarily requires the study of a great many emulsions under practical conditions. The important theoretical aspect is that it demonstrates the possibility of predicting the relative stabilities of a series of emulsions from the study of the properties of the protective films on single emulsion droplets. This is in itself a novel confirmation of the correctness of the modern adsorption film theory.

Another simple confirmation of the adsorption film theory is afforded by the comparison of the behavior of unprotected oil droplets and droplets from

a stable emulsion. Droplets formed by shaking olive oil with pure water, explode immediately upon being touched by the advancing interface. (Fig. 3 I). Droplets with gelatin as the protective agent show types of behavior such as illustrated by Fig. 3 IV–VIII. Finally in this connection, the very fact that a droplet may pass into the oil phase in which it is freely soluble and still maintain its integrity is certain evidence that a protective film is present over its surface. "Surface tension," "viscosity" and "hydration" theories of emulsion stability [44] fail to account for this phenomenon.
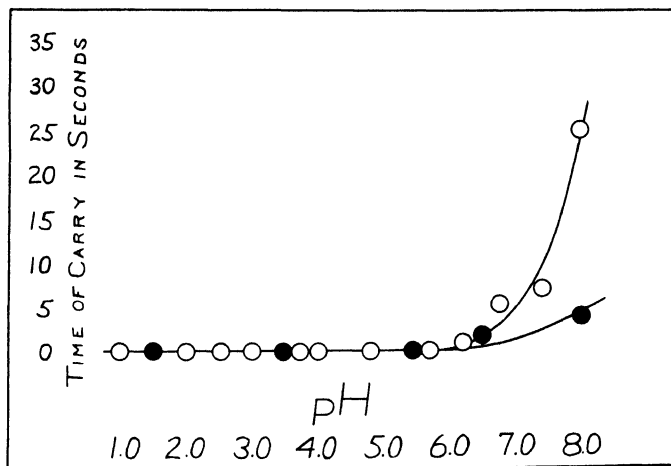
FIG. 5

Variation with pH of the average time of carry of fat droplets from cream before advancing films of triolein (circles) and mineral oil (solid dots).

The Interfacial Behavior at Different pH Values of Fat Droplets from Cream

The experiments described in this section were carried out in the same manner as those in connection with the study of the interfacial behavior at different pH values of olive oil droplets emulsified with gelatin, with the exception that one drop of cream was added to ten cc. portions of the buffer solutions rather than two drops. The results are shown graphically in Fig. 5 which compares the average times of carry of free floating droplets by the interface at the different pH values. Each of the points obtained with triolein as the interfacial oil (circles) represents a composite of observations on several hundred droplets from at least ten different stock emulsions. A series of comparative observations was made using a mineral oil (commercial "Nujol") as the interfacial oil. The behavior of freely floating droplets is compared in the case of fat droplets from cream, because a majority of the droplets are of this type. The results are therefore referred to Fig. 3 I, II, and III. To obtain the dilute emulsions at pH 1.0, the drop of cream was added to tenth normal hydrochloric acid and to obtain that at pH 1.5 it was

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[44] See Clayton: loc. cit., Chapter III.

added to a tenth molecular hydrochloric acid-sodium chloride mixture of the proper acidity. The other dilute emulsions were obtained with buffer solutions, those at pH 3.6 and above being tenth molal acetate or phosphate buffer solutions.

Immediate "explosion" took place in all cases between pH 1.0 and pH 6.0. The corresponding times of carry are therefore zero and the behavior is illustrated by Fig. 3 I. Low protective power due to low resistance of the films to disruption by the interfacial forces and possibly also to relatively low film hydration is indicated over this range. The most important point from the point of view of the present paper is the marked difference in behavior as compared with that of olive oil droplets with gelatin films under the same conditions. This comparison clearly demonstrates the possibility of differentiating different types of emulsion droplets by means of the interfacial method. The differences observed are presumably due to differences in the protective films in the two cases.

The first signs of resistance to disruption are observed just above pH 6.0 both with triolein and with "Nujol." The interface either appears to pause for a fraction of a second after making contact with a droplet before "explosion" occurs, or the droplet is carried ahead by the interface for a moment and then "explodes." There is a gradual increase in the average time of carry up to pH 8.0. This increase is much greater when triolein is used as the interfacial oil that when "Nujol" is used, permanent carry (Fig. 3 III) being frequently observed at pH 8.0.

The question of the variation of the interfacial tension at the advancing triolein interface with pH is presumably of great importance here, because the variations in interfacial behavior which are observed all occur at pH values greater than 6.0. The results of Hartridge and Peters which have been discussed in a previous section, indicate that a marked lowering in the interfacial tension might well be expected in this pH range. The question then exists as to what extent the variations in interfacial behavior observed with triolein as the interfacial oil are due to variations in the film properties with pH, and to what extent they are due to corresponding changes in the advancing interface. The fact that similar, though less marked, changes are observed when a mineral oil is used as the interfacial oil indicates that the results with triolein result from both causes.

It is a familiar fact that butter may be more readily separated from sour cream than from sweet cream.[45] The pH of fresh milk is about 6.6 and that of cream for churning usually varies down to about pH 4.8.[46] The results of the observation of the interfacial behavior of milk fat droplets over this pH range indicate a probable accompanying lowering of the resistance of their protective films to disruption. This comparison of the interfacial behavior of emulsion droplets with the stabilities of emulsions under the same conditions affords another indication of the possible use of the interfacial method in practical emulsion studies.

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[45] Heineman: loc. cit., page 602.
[46] Personal communications to the writer.

Guthrie and Sharp[47] have recently reported the effect of variation of pH upon the churning time of cream under various conditions. Their results, when the water of the cream was made o.1 N with respect to sodium chloride may be compared with Fig. 5 since the results shown there were obtained with milk fat droplets in o.1 N buffer solutions of sodium salts. Under these conditions they found a clearcut decrease in churning time on going from about pH 8.o to about pH 4.o with only a slight increase over the range pH 4.o–pH 2.o, entirely in accord with the results described in this section.

Summary

It has been demonstrated that the Mudd interfacial technique affords interesting possibilities as a method for the investigation of the properties of protective protein films on single oil-in-water emulsion droplets. The general types of behavior shown by oil droplets with protective protein films when examined by means of this technique have been described and interpreted. This material points the way to its use in emulsion research.

A comparison of results with olive oil droplets with protective films of gelatin and with fat droplets from cream clearly demonstrates the usefulness of the method in observing differences in the properties of droplets from different emulsions. The differences observed are presumably due to differences in the protective protein films in the two cases.

The experimental work has afforded several novel confirmations of the correctness of the modern adsorption film theory of emulsion stability.

It has been found possible to predict the relative stabilities of a series of emulsions from a study of the properties of the protective films on single emulsion droplets as would be predicted on the basis of the modern adsorption film theory. This result points to the possibility of the use of the interfacial technique in practical emulsion work.

Under certain conditions a means is apparently afforded of making a direct experimental comparison of the relative states of surface hydration of oil-in-water droplets with protective protein films. Assuming the interpretation of the observed phenomena to be correct, it has been found possible to demonstrate that the surface hydration of protective films of gelatin on olive oil droplets varies in the same general manner with pH over the range studied as does the hydration of gelatin particles in solution.

Under certain conditions also, the interfacial technique affords a means of studying the resistance of protective protein films on single oil-in-water emulsion droplets to disruption under the action of interfacial forces and simple mechanical stretching and compressing forces.

Combining the abilities described in the two preceding paragraphs, it has been shown to be possible to differentiate experimentally between two important protective properties of protein films, their resistance to disruption under the action of interfacial and mechanical forces on one hand and their state of hydration *per se*. This experimental differentiation has not hitherto been accomplished.

*The Gladwyne Research Laboratory, Gladwyne, Pa., and
    the Department of Industrial Research, University of Pennsylvania.*

[47] Guthrie and Sharp: J. Dairy Science, **14**, 1 (1931).

THE SURFACE TENSIONS OF BINARY MIXTURES OF FOUR VOLATILE FATTY ACIDS[1]*

BY ELLIS I. FULMER AND JEROME ANDES

Accurate studies in the field of fermentation are at present handicapped by the lack of adequate quantitative analytical procedures. The problem is complicated by the fact that there are produced in most fermentation processes a large variety of products representing a number of homologous series. Prominent among such products are the volatile fatty acids. Until recently, the available methods for the analysis of these compounds have been based upon fractional distillation; that is, they are modifications of the Duclaux procedure. These methods have been reviewed by Moore and Fulmer[1] who proposed a method for the analysis of formic and acetic acids, based upon a conductometric titration with ammonium hydroxide. The conductivity method has been further extended to binary mixtures of formic, acetic, propionic, and n-butyric acids, by Fulmer, Moore, and Foster.[2] These authors found that the antilogarithms of the specific conductivity ($\times 10^3$) of a binary mixture at 0.01 N are a linear function of the composition. By the use of the relations developed the percentage composition of a binary mixture of any of the four acids may be calculated within an average difference from the theoretical of 0.2%.

Behrens[3] partitioned mixtures of the volatile acids between diethyl ether and water and proposed a method of analysis based on the partition coefficient. Werkman[4,5,6,7] has simplified this procedure and has found isopropyl ether a better immiscible solvent than the diethyl ether. He has likewise extended the technique to a provisional analysis of mixtures of three acids.

It is evident that it is advisable to make studies of further properties of mixtures of these acids. This communication is concerned with a study of the surface tensions of binary mixtures of formic, acetic, propionic, and n-butyric acids at 0.2 and 0.1 normal concentrations.

The work on the surface tensions of aqueous solutions of the volatile fatty acids is summarized by Harkins and Young,[8] and a general review will not be necessary in this paper. Of special interest is a paper by Szyskowski[9] in which he studied by the capillary rise method the surface tension of the volatile fatty acids. He found the following relation to hold:

$$\triangle = \frac{S_M - S_L}{S_L} = b \log (c/a - 1) \tag{1}$$

in which, $\quad$ c = molar concentration of acid

$\quad\quad\quad$ S_L = surface tension of the solution

$\quad\quad\quad$ S_M = surface tension of the solvent

$\quad\quad\quad$ b and a are constants

Freundlich[10] states that at high concentrations 1 may be neglected as compares to c/a and hence:

$$\triangle = \frac{S_M - S_L}{S_M} = s\ c^{1/n} \tag{2}$$

or $\qquad\qquad\qquad$ $\log \triangle = 1/n \log c + \log s$ $\qquad\qquad\qquad$ (3)

The graphs according to equation (3), give under these conditions straight lines for nine acids, in each of which the value of $1/n$ is about 0.7. Hence, the value of log s is a direct measure of the place of the acid in Traube's series.

There are many methods for the determination of surface tensions, the most commonly used ones being the capillary rise, the drop-weight, and the pull-on-ring procedures. A general discussion of various techniques of special interest in biological work is given by Buchanan and Fulmer.[11] The "pull-on-ring" method is the most commonly used by biological workers because of its development and extensive employment by DuNoüy.[12,13,14,15] In the work cited it has been assumed that the surface tension is a linear function of the grams pull on the ring, or

$$\gamma_1 = \frac{Mg}{4\,\pi\,R} \tag{4}$$

The instrument used is calibrated in terms of dynes per cm. on the basis of the above formula.

Harkins, Young, and Cheng[16] have shown that the above formula does not give the true surface tension, and that the following relation must be used,

$$\gamma_1 = \frac{Mg}{4\,R} \times F \tag{5}$$

where $\qquad\qquad\qquad$ $F = f\ (R^3/V,\ R/r,\ etc.)$ $\qquad\qquad\qquad$ (6)

in which $\quad$ M = pull of the ring in grams

$\quad\quad\quad$ R = radius of the ring

$\quad\quad\quad$ r = radius of wire of the ring

$\quad\quad\quad$ g = gravity constant

$\quad\quad\quad$ D = density of the liquid

$\quad\quad\quad$ d = density of the air saturated with the vapor of the liquid

$\quad\quad\quad$ V = volume of the liquid raised above the surface of the liquid

$\quad\quad\quad\quad$ = M/(D − d)

Recently Harkins and Jordan and Jordan[17] have extended this work and have published extensive tables of F for various values of R^3/V and R/r. They used a chainomatic balance and point out many precautions necessary for obtaining accurately the pull on the ring. With this technique thus developed, and by the use of the equation (6), they regard this method as precise. They found results of the application of equation (5) as much as 30% too high for some low surface tensions, and 30% too low for certain interfacial tensions.

This work here reported is concerned with the surface tension measurements of 0.2 and 0.1 normal solutions of formic, acetic, propionic, and n-butyric acids, and the six possible binary combinations of these acids at each normality. The acids used were Merck's highest quality, redistilled before using. Their strength was determined by titration with NaOH using phenolphthalein as an indicator.

A chainomatic surface tension balance was employed. A 4-inch petri dish was used to contain the liquid to be measured. This obviated the necessity of corrections for curvature, etc. The dish was supported by means of wire clips in an 8-inch crystallizing dish, which served as a constant temperature bath. Measurements were made in a room not varying over one degree from 25° Centigrade, so little difficulty was experienced in keeping the bath at 25°—the temperature at which the measurements were made. The water in the constant temperature bath was mixed by hand, and since the only change in temperature occurring was a cooling effect, the constant temperature was maintained by adding small amounts of water (at 30°) as needed. A twenty cc. sample of material was used for each surface tension measurement.

Absolute cleanliness is imperative. The petri dishes in which the measurements were made were cleaned with cleaning solution between every determination. This was found to be absolutely necessary for reproducible results. Also all bottles and pipettes used were kept absolutely clean. The wire stirrup, or ring, was flamed between every reading. The same stirrup was used throughout, and was handled with great care, every precaution being taken to avoid bending or twisting of any kind. After the liquid was poured into the petri dish, sufficient time was allowed to elapse for the temperature to become constant. This usually took about 2–3 minutes. Then readings were taken until they became constant. Generally only about four or five readings were necessary. Careful technique had to be acquired in lowering the dish and moving the chainomatic weight in the proper ratio. The pointer was kept at zero and the weight carefully added until the ring "broke loose." This maximum pull was recorded. Measurements on water were made from time to time and consistently checked to the fourth place. The value for water was found to be 72.17 dynes as against 71.97 as determined by Harkins and Jordan.[17]

The results obtained for binary mixtures of the four acids at 0.2N and 0.1N are given in Tables I and II, the letters F, A, P, B, are the initial letters of the acids used. Values for γ_1, by equation (4) and γ by equation (5) are also tabulated. Values of F were interpolated from the data of Harkins and Jordan.[17] For the ring used R = 0.631 cm. and r = 0.00157 cm. from which R/r = 40.6. In eq. (6) is given the term R^3/V. In our data the value of D−d is so nearly equal to unity that R^3/M was used in place of R^3/V. It has been argued by some workers that while the factor, F, should be theoretically considered that errors in neglecting this factor would be practically constant. The values of $\gamma_1 - \gamma$ in the tables show this statement to be incorrect, the correction varying from 1.08 dynes to 2.48 dynes, the error increasing numerically with decrease in surface tension values, from which it is apparent that the percent error is large. The values of γ for these mixtures are given on graphs 1 and 2. These graphs may be used directly for the analysis of binary mixtures of the acids concerned. The mixture is made up to exactly 0.2 N or 0.1 N and the surface tension (γ) determined. Dilution of the unknown mixture with a known binary mixture of the acids at the same normality will not show a change in surface tension for that combination present in the unknown.

It is evident that the surface tension of a binary mixture is not a linear function of the composition. It was found that the data fitted the exponential function,

$$y = 10^{mx} + c \tag{7}$$

or

$$\log (y - c) = mx + \log a \tag{8}$$

The value of c in equation (8) may be approximated by the following relation,

$$c = y_1 + \frac{(y_1 - y_2)^2}{2y_2 - y_1 - y_3} \tag{9}$$

in which y_1, y_2 and y_3 are values of the function for equal increments of the variable. It developed a value of c = 45 gave an entirely satisfactory fit for all binary mixtures at both normalities. This fact is very interesting in view of the fact that 45 is the difference between the value of the surface tension of the pure solvent and the average value for the pure acids. Whether this relation is general remains to be determined.

In Tables I and II are given values for γ_3 as calculated by the relation,

$$\log (\gamma - 45) = m\% + b \tag{10}$$

In the tables are also given for m and b as well as for $\gamma - \gamma_3$. It is evident that the relation of equation (10) gives remarkable agreement with the determined values.
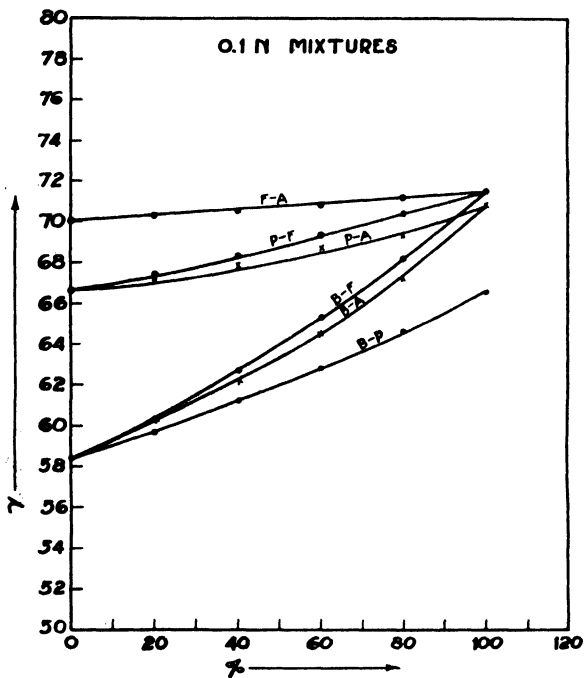
FIG. 1
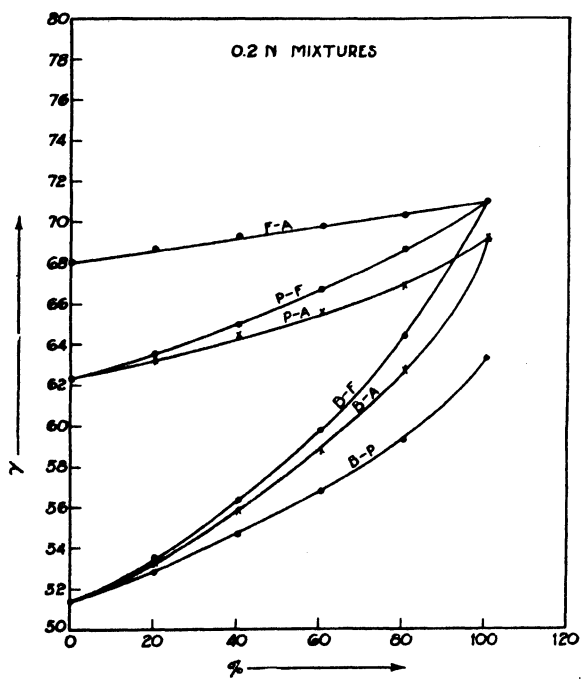
FIG. 2

TABLE I

Surface Tensions for 0.2N Binary Mixtures of Four Volatile Fatty Acids

Mixture	%	M	γ_1	γ	$\gamma_1 - \gamma$	γ_3	$\gamma - \gamma_3$
F — A	0	0.5675	69.48	68.16	1.32	68.12	+0.04
m = 0.000490	20	0.5715	69.97	68.71	1.26	68.61	+0.10
b = 1.3642	40	0.5755	70.46	69.26	1.29	69.19	+0.07
	60	0.5798	70.98	69.85	1.13	69.75	+0.10
	80	0.5842	71.52	70.38	1.14	70.31	+0.07
	100	0.5889	72.10	71.02	1.08	70.89	+0.13
F — P	0	0.5232	64.05	62.25	1.79	62.26	0
m = 0.001762	20	0.5331	65.27	63.57	1.70	63.72	−0.15
b = 1.2370	40	0.5442	66.63	65.03	1.60	65.30	−0.27
	60	0.5573	68.23	66.80	1.43	67.02	−0.22
	80	0.5719	70.02	68.83	1.19	68.88	+0.05
	100	0.5889	72.10	71.02	1.08	70.89	+0.13
A — P	0	0.5232	64.05	62.26	1.79	62.26	0
m = 0.001272	20	0.5308	64.99	63.30	1.69	63.30	0
b = 1.2370	40	0.5400	66.11	64.52	1.59	64.40	+0.08
	60	0.5489	67.20	65.65	1.55	65.57	+0.08
	80	0.5577	68.28	66.84	1.44	66.82	+0.02
	100	0.5675	69.49	68.16	1.32	68.12	+0.04
F — B	0	0.4406	53.94	51.46	2.48	51.53	−0.07
m, = 0.005983	20	0.4569	55.94	53.53	2.41	53.60	−0.07
b = 0.8149	40	0.4788	58.62	56.39	2.23	56.33	+0.06
	60	0.5045	61.76	59.73	2.03	59.76	+0.03
	80	0.5398	66.09	64.30	1.79	64.65	−0.35
	100	0.5888	72.08	71.02	1.07	70.89	+0.13
A — B	0	0.4406	53.94	51.46	2.48	51.53	−0.07
m = 0.005493	20	0.4557	55.79	53.34	2.45	53.41	−0.07
b = 0.8149	40	0.4750	58.15	55.94	2.21	55.82	+0.12
	60	0.4985	61.03	58.96	2.07	58.95	+0.01
	80	0.5261	64.41	62.67	1.84	62.96	−0.29
	100	0.5675	69.48	68.16	1.32	68.12	+0.04
F — B	0	0.4406	53.94	51.46	2.48	51.53	−0.07
m = 0.004221	20	0.4515	52.28	52.84	2.44	52.93	−0.09
b = 0.8149	40	0.4657	57.02	54.68	2.34	54.63	+0.05
	60	0.4815	58.95	56.77	2.18	56.70	+0.07
	80	0.5007	61.30	59.28	2.02	59.21	+0.07
	100	0.5232	64.05	62.26	1.79	62.26	0
Pure Water		0.5973	73.64	72.19	1.47	71.97	+0.22

Surface Tensions of 0.1N Binary Mixtures of Four Volatile Fatty Acids

Mixture	%	M	γ_1	γ	$\gamma_1 - \gamma$	γ_3	$\gamma - \gamma_3$
F − A	0	0.5818	71.23	70.09	1.14	70.01	−0.08
m = 0.000267	20	0.5832	71.40	70.26	1.14	70.30	+0.04
b = 1.3961	40	0.5852	71.64	70.57	1.07	70.60	+0.03
	60	0.5877	71.95	70.87	1.08	70.89	+0.02
	80	0.5903	72.26	71.18	1.08	71.20	+0.02
	100	0.5932	72.62	71.61	1.01	71.51	−0.10
F − P	0	0.5554	68.00	66.50	1.50	66.61	+0.11
m = 0.000929	20	0.5613	68.72	67.34	1.38	67.51	+0.17
b = 1.3293	40	0.5684	69.59	68.33	1.26	68.45	+0.12
	60	0.5760	70.52	69.32	1.20	69.42	+0.10
	80	0.5844	71.55	70.40	1.15	70.45	+0.05
	100	0.5932	72.62	71.61	1.11	71.51	−0.10
A − P	0	0.5554	68.00	66.50	1.50	66.61	+0.11
m = 0.000662	20	0.5598	68.54	67.10	1.44	67.25	+0.15
b = 1.3293	40	0.5650	69.17	67.79	1.38	67.91	+0.12
	60	0.5705	69.85	68.59	1.26	68.59	0
	80	0.5761	70.53	69.33	1.20	69.29	−0.04
	100	0.5818	71.23	70.09	1.14	70.01	−0.08
F − B	0	0.4938	60.45	58.34	2.11	58.37	+0.03
m = 0.002983	20	0.5086	62.26	60.27	2.00	60.32	+0.05
b = 1.1239	40	0.5264	64.45	62.71	1.74	62.58	−0.13
	60	0.5464	66.91	65.30	1.61	63.15	−0.15
	80	0.5675	69.48	68.16	1.32	68.11	−0.05
	100	0.5932	72.62	71.61	1.01	71.51	−0.10
A − B	0	0.4938	60.45	58.34	2.11	58.37	+0.03
m = 0.002716	20	0.5083	62.23	60.24	1.99	60.09	−0.15
b = 1.1239	40	0.5230	64.03	62.09	1.93	62.23	+0.14
	60	0.5400	66.11	64.46	1.65	64.37	+0.11
	80	0.5595	68.50	67.06	1.46	67.21	+0.15
	100	0.5818	71.23	70.09	1.14	70.01	−0.08
P − B	0	0.4938	60.45	58.34	2.11	59.37	+0.03
m = 0.002054	20	0.5037	61.67	59.63	2.04	59.71	+0.02
b = 1.1239	40	0.5150	63.05	61.16	1.89	61.19	+0.03
	60	0.5275	64.58	62.84	1.74	62.82	−0.02
	80	0.5413	66.27	64.61	1.66	64.63	+0.02
	100	0.5554	68.00	66.50	1.50	66.61	+0.11

Summary

1.   The surface tensions of binary mixtures of formic, acetic, propionic and n-butyric acids at 0.2 N and 0.1 N have been determined by use of a chainomatic tensiometer.   The values were calculated by the relation

$$\gamma = \frac{Mg}{4\,\pi\,R} \times F$$

using the values of F calculated by Harkins and Jordan.

2.   For all binary mixtures at both normalities the surface tension is related to percent composition by the relation,

$$\log{(\gamma - 45)} = m\% + b$$

References

[1] Moore and Fulmer: Iowa State Coll. J. Sci., **4**, 1 (1929).

[2] Fulmer, Moore and Foster: J. Phys. Chem., **35**, 1227 (1931).

[3] Behrens: Z. anal. Chem., **69**, 97 (1926).

[4] Werkman: Ind. Eng. Chem., (Anal. Ed.) **2**, 302 (1930).

[5] Werkman: Iowa State Coll. J. Sci., **4**, 459 (1930).

[6] Werkman: Iowa State Coll. J. Sci., **4**, 1 (1930).

[7] Werkman: Iowa State Coll. J. Sci., **5**, 121 (1930).

[8] Harkins and Young: Int. Crit. Tables, p. 447, et seq.

[9] Szyskowski: Z. physik. Chem., **64**, 385 (1908).

[10] Freundlich: (trans. by H. S. Hatfield) "Colloid and Capillary Chemistry."

[11] Buchanan and Fulmer: "Physiology and Biochemistry of Bacteria," Vol. I (1928).

[12] DuNoüy: J. Gen. Physiol., **1**, 521 (1918-1919).

[13] DuNoüy: Phil. Mag., **6**, 48, 254 (1924).

[14] DuNoüy: Science, **59**, 580 (1924).

[15] DuNoüy: "Surface Equilibria of Colloids" (1926).

[16] Harkins, Young and Cheng: Science, **64**, 333 (1926).

[17] Harkins and Jordan: J. Am. Chem. Soc., **52**, 1751 (1930).

ACTIVATED SILICA GEL[1]

The Relation of Activity to Water Content
and Temperature of Activation

BY F. E. BARTELL AND E. G. ALMY[*]

Introduction

Preparation of Activated Silica. Silica gel is usually prepared by treating sodium silicate of a suitable concentration with an acid such as hydrochloric acid, or with certain salts, such as ferric chloride, which are acid in reaction. The gelatinous mass thus formed is broken up, washed free from salts, and dried until the gel becomes hard and glassy in appearance. The water content at this stage will vary with the method of preparation but is nearly always well above five percent. Finally, the gel is heated to a moderately high temperature (150° C. to 400° C.), usually in a current of dry air. This process, known as activation, decreases still further the water content of the gel and increases greatly its adsorptive capacity. While the term "activated silica" is commonly applied to this product the term "silica gel" has often been used interchangeably with it. The latter term is also used to indicate not only activated gel but also gel which may contain much more water.

The preliminary drying of silica gel has been studied by van Bemmelen,[2] Zsigmondy[3] and others. This study is generally interpreted to show, (1) that the gel as it is first formed consists of an interlacing mass of silica threads the spaces between them being filled with capillarily held water, and (2) that the preliminary drying drives out at least the major portion of this water. During the preliminary drying the gel shrinks in volume and, when ready for the final activation, is generally believed to consist of a mass of interlacing silica threads forming a multitude of micropores. The effective diameters of these pores have been estimated to be approximately 5 mμ.

Holmes[4] has found that the shrinkage of the gel upon drying might be somewhat lessened if the gel, while still containing a relatively large percentage of water (60%) be kept at a high temperature (approaching 100° C.) and held in such a manner that water could not evaporate from the system. He believes that this process "sets" the framework so that upon subsequent drying the contraction is less than for gels not treated in this manner.

Kistler[5] has succeeded in removing the water from silica gel with no attendant decrease of volume. This is accomplished by first displacing the water by an organic liquid miscible with it, and then by replacing the first

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[2] Van Bemmelen: "Die Absorption," 205 (1910).
[3] Zsigmondy: "Kolloidchemie," 150 (1912).
[4] Holmes: Ind. Eng. Chem., **17**, 280 (1925).
[5] Kistler: Nature, **127**, 741 (1931).

organic liquid by another which has a very low critical temperature. If the gel is then heated in an autoclave to a temperature higher than the critical temperature of this liquid, and the pressure is slowly released, the organic liquid is removed but the total volume of gel is not appreciably altered. Gels thus prepared, called aerogels, have a very low apparent density, they retain the shape of the original gel and may under proper conditions be rehydrated to the original state. These gels, like those of van Bemmelen, always contain small amounts of residual water. In the case of the aerogels any attempt to remove this water results in a crumbling of the sample. This investigation has given good evidence that freshly prepared silica gels have a definite internal structure or framework. During the ordinary process of drying of such gels, they shrink to a small fraction of the original volume which indicates that the structural framework must collapse.

Structure of Activated Gel. Quite definite evidence of the existence of capillary pores in silica gel has also been obtained by Fells and Firth.[1] They found that when a gel prepared by the usual method is allowed to dry before the salt is washed out, long needles of sodium chloride grow out from the surface of the gel as it shrinks. As the drying and shrinking continue these needles break off and a new crop of finer needles appears. This evidence, they feel, indicates the existence of a capillary pore structure. The salt solution is squeezed out through the pores as the gel shrinks, the water evaporates, and the salt is deposited as needles. Further shrinkage contracts the pores and snaps off the first formed needles, whereupon a growth of finer needles is noticed as the gel continues to dry. They found that there was no difference between the finally obtained gels whether prepared by washing out the salt before sintering or after sintering.

Jones,[2] likewise, has obtained some evidence that silica gel must possess capillary pores. In an investigation upon adsorption from solution by silica of varying degrees of dispersivity, he found that silica gel adsorbed more of the solute than did less highly dispersed ground quartz. He concluded, however, from the shapes of the adsorption isotherms that the increased adsorptive capacity of the gel over that of the crystalline material could not be accounted for by the greater specific surface alone, but that fine capillary pores must exist within the gel which in some manner increase the adsorptive capacity.

It has been reported by Kyropoulos[3] and others that silica gel shows no X-ray diffraction pattern and, therefore, that the silica constituting the framework of the structure is amorphous. Quite recently, however, Krejci and Ott[4] obtained X-ray photographs of silica gel, that had never been treated at temperatures higher than 100°, and found the pattern of cristobalite to be distinctly visible. They believe that at least some crystalline nuclei are present in the gel.

[1] Fells and Firth: J. Phys. Chem., **29**, 241 (1925).

[2] Jones: J. Phys. Chem., **29**, 327 (1925).

[3] Kyropoulos: Z. anorg. allgem. Chem., **99**, 197 (1917).

[4] Krejci and Ott: J. Phys. Chem., **35**, 2061 (1931).

Patrick, Frazer, and Rush[1] have investigated the structure of silica gel as it varies with the temperature of activation. They studied the apparent densities, the adsorptive capacities for CCl_4 vapors, and the X-ray diffraction patterns of samples of gel that had been heated at successively increasing temperatures, each for a period of two hours. For temperatures up to 800° C. they found that the density and adsorptive capacity remained constant. As the temperature of activation was increased from 800° to 1000° C., the density increased while the adsorptive capacity decreased to a minimum. This, it would seem, indicated a closing of capillary pores in the system, thereby decreasing the capillary volume as well as the effective surface area. None of these gels were found to exhibit diffraction patterns characteristic of crystalline silica. It was found necessary to heat the gel at 1100° C. for three days to produce sufficient crystallization to give visible diffraction patterns. Unfortunately the water content of the various samples was not determined.

The evidence obtained from the literature indicates that in activated silica we are dealing with the partially collapsed framework of a gel. The interstices between the interlacing mass of threads have become very small during the collapse so that they form microcapillary spaces. The effective radii of these pores are not the same throughout the gel but grade from a maximum, determined by the method of preparation, down to a radius of molecular dimensions. The internal surface area of such a system is very large. The solid forming the framework is silica, usually considered to be amorphous, although there is now some evidence to support the view that there are at least some crystalline nuclei present. It is possible that the silica is entirely present in the form of colloidal crystals—crystals so small that their existence has been overlooked in the earlier work. If the activated silica is heated for some time at temperatures of 1000° C. to 1100° C. there is an increase in the crystallinity of the substance and at the same time the capillary volume is apparently greatly reduced.

Relation of Water Content to "Activity." A fact frequently overlooked in discussions of activated silica is that the product nearly always, if not always, contains small amounts of water. This water may vary considerably in amount with the method of preparation of the gel, but its removal beyond a given point is accompanied by a great decrease in the activity of the gel. Fells and Firth[2] have found that gels prepared at several different temperatures had in each case about the same water content after a final heating at 600° C. Gel initially prepared at 0° C. presented an exception for in this case the final water content was appreciably lower than that of those gels prepared at higher temperatures. This gel adsorbed water vapor more slowly than did the others and its final adsorption capacity was less.

Berl and Burkhardt[3] likewise found that gels which retained the lesser amounts of water after a given final treatment adsorbed the lesser amounts of water vapor. They noted also that gels which adsorb the lesser amount of

[1] Patrick, Frazer, and Rush: J. Phys. Chem., **31**, 1511 (1927).

[2] Fells and Firth: J. Phys. Chem., **29**, 241 (1925).

[3] Berl and Burkhardt: Z. anorg. allgem. Chem., **171**, 102 (1928).

water vapor give the lower heats of wetting. These investigators obtained their gels of different water content by varying the concentrations of the mixtures used in their preparation.

Ray[1] prepared gels of different water contents by dehydrating samples of a given preparation at successively higher temperatures. He noticed that the water content decreased linearly with increasing temperatures of activation but failed to state at what temperatures he treated the various samples to obtain the given degree of dehydration. He investigated the relation of activity to water content by comparing the adsorptive capacities of the various samples for nitrogen peroxide. Within the range 6.8 to 4.7 percent of water the amounts of N_2O_4 adsorbed per gram of gel were nearly constant. At lower water contents, such as at 3.3 percent, there was a falling off of adsorptive capacity. Ray also found evidence (unfortunately indirect) to indicate that the N_2O_4 reacted with the gel water to form HNO_3 and N_2O_3, the HNO_3 remaining in the gel in place of the water that was originally present. The adsorptive capacity of the gel was only slightly diminished by this replacement.

McGavack and Patrick[2] likewise found that the adsorption of a water soluble gas (SO_2) by silica gel was not affected by changing the water content between the limits of about 5 to 8 percent, but Patrick and Davidheiser[3] found that even small differences in water content produced large variations in the adsorptive capacity of silica gel for NH_3.

Manner of Retention of the Bound Water. The investigations cited above, though dealing with the amount of water in activated silica, have contributed but little in answer to the question as to how such water is retained. There appear to be three possible ways in which this bound water may be held in the gel. (1) The water may be condensed in very fine capillary spaces. (2) It may be adsorbed as a continuous film over the surface of the solid silica. (3) It may constitute an integral part of the gel framework, even to the point of being present in chemical combination.

Jones[4] expressed the view that the last 6 to 8 percent of the water is held in such fine capillary spaces that when it is driven out, the voids so formed cannot be occupied by molecules of other adsorbates. He based this conclusion on the fact that each of different gels with water contents of from 6.2 to 3.4 percent adsorbed the same amounts of acetic acid from a given acetic acid-gasoline solution. At a water content of one percent, he found, however, that the adsorptive capacity was much less than in the other samples. This he attributed to a breakdown of the gel structure at the high temperature necessary to dehydrate so completely.

The view that the water is adsorbed as a continuous film over the solid framework of the gel has at times received support. Patrick and Grimm[5] in

[1] Ray: J. Phys. Chem., **29**, 74 (1925).

[2] McGavack and Patrick: J. Am. Chem. Soc., **42**, 946 (1920).

[3] Patrick and Davidheiser: J. Am. Chem. Soc., **44**, 1 (1922).

[4] Jones: loc. cit.

[5] Patrick and Grimm: J. Am. Chem. Soc., **43**, 2144 (1921).

their work on the heat of wetting of silica gel assumed that the gel particles actually presented a water surface to their surroundings. With this assumption they were able to make calculations of the area of the water surface which was exposed to the wetting liquids. Using the heats of wetting of water, benzene, carbon tetrachloride and aniline they obtained values for the specific area that showed good agreement. The heat of wetting of silica by alcohol was found to be higher than that by water. To explain this fact the authors proposed the theory that alcohol is insoluble in the gel water because of the highly concave meniscus of the water which was held in the fine capillary spaces, and that a water-alcohol interface is formed. To postulate such an abnormal behavior of water toward one liquid immediately after using the normal value of its interfacial tensions against other liquids is so inconsistent that the attempt to explain the heat of wetting phenomena on the basis of the exposure of a water surface by the gel seems scarcely justified.

As a third possibility it may be postulated that the water forms an integral part of the gel framework. This would amount essentially to chemical combination of the water with the silica, differing from chemical combination as we ordinarily think of it in that stoichiometric proportions are not involved. Water molecules would be thought of as forming connecting links between particles of the solid so that when they are finally removed the structure would collapse. There has been no experimental evidence for such a view except the fact that the adsorptive capacity and the heat of wetting are greatly decreased if all the water is driven from the gel.

Summarizing, it may be stated that the evidence from the literature concerning the manner in which water is contained in activated silica is far from conclusive. Gel that is active probably always contains some water but there are decided differences of opinion both as to how this water is retained and as to the relation of the water content to the activity of the gel.

The purposes of the present investigation, then, were (1) to determine the conditions necessary for activating silica reproducibly to any desired degree, (2) to determine the relation of the amount of water in silica gel to its activity, (3) to obtain data that will indicate the manner of retention of water in the gel, and (4) to throw further light on the subject of the structure of silica gel.

The method employed in attacking these problems was to study the interrelations between temperature of activation, time of activation, water content of the resulting product, and its heat of wetting. The heat of wetting values of a series of gels were taken as representing their relative activities. The wetting agent in all the cases reported in this paper was water but an extensive series of measurements (as yet unpublished) has shown that the ratio of heats of wetting of one sample of gel by different liquids is the same as the ratio of heats of wetting of any other gel by those liquids, irrespective of differences in activity or in method of preparation of the gel. Thus, the same *relative* activities would have been obtained had any other liquid which wets silica completely been substituted for water in these experiments, and the same conclusions would have been drawn.

Experimental

Apparatus. With but one change, the calorimeter used, Fig. 1, was the same as described by Bartell and Fu.[1] A rotating propeller was used as a stirrer in place of the ring stirrer described by them. The calorimeter vessel was a Dewar flask of about 150 cc. capacity, fitted with a ground glass stopper. Through this stopper was passed a Beckmann thermometer, the mercury sealed stirrer shaft, a small heating coil, and the holder for the bulbs of powder to be used. The calorimeter was placed in an air bath, the temperature of which could be regulated to $\pm.05°C$.

The method of operation was as follows: Approximately 60 cc. of the liquid to be used was placed in the calorimeter vessel, a small thin walled bulb containing the sample of silica was sealed to the holder which extended through the cover, the apparatus was assembled, and the stirrer started. When the calorimeter was at the temperature of the air bath, as evidenced by constant readings of the thermometer for at least thirty minutes, a small measured current was sent through the heating coil for a known length of time, the time being determined with a stop watch. The temperature rise was noted and the heat capacity, C_p, of the entire assembly calculated in calories per degree, using the formula:

$$C_p = \frac{i^2 rt}{TJ}$$

i represents the current, measured by a calibrated milliammeter; r, the resistance of the coil; t, the time; T, the temperature rise, and J, the mechanical equivalent of heat.

The apparatus was next allowed to cool to the temperature of the bath, and the bulb containing the powder was broken by gently pushing it against the side or bottom of the vessel. When the powder was wet by the liquid the temperature increase was again noted, and the heat of wetting calculated in calories per gm. from the equation:

$$-Q = \frac{T}{W} C_p$$

W represents the weight of the sample.

The heat capacity of the calorimeter plus its contents was always redetermined after the temperature rise due to wetting had been measured and the average of the two (or more) determinations was used as the C_p value in the above equation.

By suitably choosing the time interval used in determining the heat capacity, the temperature rise in the calibration could be made approximately the same as that occurring in the determination, thus minimizing the heat radiation error. In every case the full heat effect was developed in less than two minutes. Preliminary measurements were made to demonstrate that the determined heat capacity was constant throughout a considerable range of energy input, and that the temperature rise occasioned by the wetting of

[1] Bartell and Fu: Colloid Annual, **7**, 135 (1929).

silica was directly proportional to the weight of the sample throughout a range of weights considerably greater than those finally used and reported. In a large number of determinations of the heat of wetting, the average deviation was ±0.15 calories per gram.

Materials. The silica used was prepared according to the direction of Bartell and Fu. A good grade of water glass was diluted to a specific gravity of 1.025, and neutralized with 1:1 HCl. Before the mixture had set to a gel, saturated nickel nitrate solution was added in the proportion of 200 cc.

MERCURY SEAL
THERMOMETER
HOLDER
GROUND JOINT
SiO₂
STIRRER
NICHROME HEATER

FIG. 1

DEHYDRITE BULB
GROUND GLASS JOINT
SILICA GEL
SCREW CLAMP
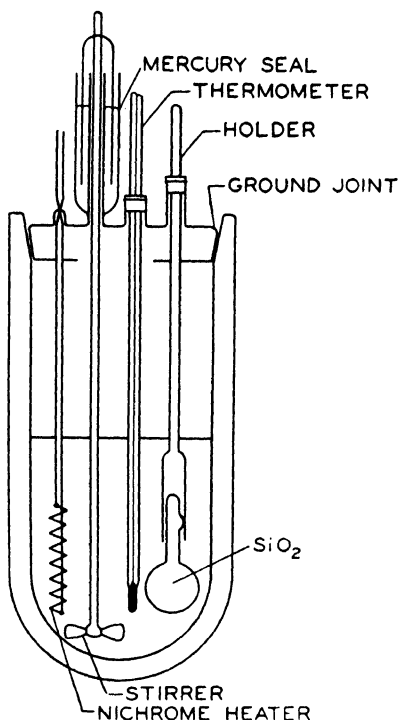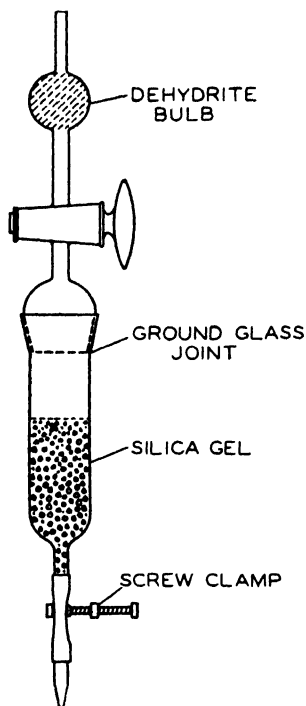
FIG. 2

nickel nitrate to 1,000 cc. of silicic acid solution. The mixture very soon set to a solid green gel, and was allowed to synerize at 90° C. for several days. When the gel appeared to be thoroughly dried it was washed with water and HCl until the wash water no longer tested for Ni^{++} with dimethyl glyoxime reagent. It was then heated at 250° in a quartz vessel for two hours and poured immediately into cold conductivity water. This last treatment, which was repeated several times, caused the larger granules to split apart and aided in removing the remaining traces of HCl. The gel was then ground and sifted, the portion having particle sizes from 40 to 160 mesh being retained. This portion was again thoroughly washed, and was finally dried at 250° C. A quantity of this gel sufficient for all our experiments was prepared and thoroughly mixed. It was stored in open vessels in a $CaCl_2$ desiccator at 25° C. to insure uniformity of water content before the activation treatment.

The samples of gel were activated by heating in a muffle furnace to the desired temperature for a definite length of time, and were then immediately transferred to the previously dried apparatus sketched in Fig. 2. After the transfer the small calorimeter bulbs were filled rapidly through the small opening at the lower end of the device and were sealed off at once. In every case the filling of the bulbs was completed before the gel had cooled to room temperature.

The analysis for water was made by determining the loss on ignition. When the calorimeter bulbs were being filled a larger sample was also drawn off and sealed into a test tube. After it had cooled to room temperature this sample was transferred to a platinum crucible and weighed. The crucible and the contents were then ignited to constant weight. This required heating at least six hours under a bench muffle equipped with a Meker burner having an auxiliary air blast. The crucible was always placed in a dried stoppered bottle to be weighed, since otherwise the silica gained weight too rapidly on the balance pan to permit of accurate weighing.

Conductivity water was used throughout this investigation.

Measurements and Results. If reproducible heats of wetting are to be obtained it is essential that the conditions of activation be carefully controlled. Data showing the necessity of such control are given in Table I. The furnace was heated to the temperature shown in the first column and a crucible containing approximately twenty grams of the gel placed therein. The sample was removed at the end of the time shown in the second column. In the third column the heats of wetting of the various samples are given. It must not be overlooked that an appreciable time is required to heat the sample of gel and that the time shown in the table does not represent the time at which the sample was actually at the given temperature. In general, increasing either the temperature or the time of the heat treatment decreases the activ-

TABLE I

Heat of Wetting as related to Temperature and Time of Activation

Temp. °C.	Time min.	$-Q_w$ cal./gm.
800	15	14.87
825	10	13.61
900	15	13.13
900	30	11.98
930	10	11.98
1000	1	16.41
1000	2	13.97
1000	3	13.50
1000	4	11.63
1000	5	11.66
1000	7	11.49
1000	15	11.53

ity of the gel. This indicates that possibly the water content of the gel is an important factor in determining its activity. The next series of experiments was designed to test this view.

The temperature of activation was kept constant at 220° C. and the time of heating was varied. The water content and heat of wetting corresponding to each treatment was measured. The same procedure was followed at 500° and 800° C. The results obtained are tabulated in Table II, and plotted in Figs. 3 and 4.
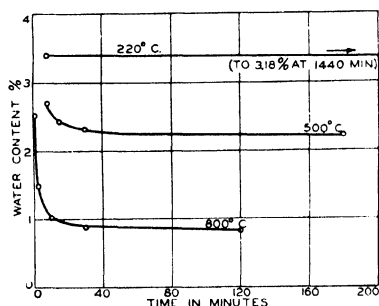
FIG. 3
Relation of Water Content to
Time of Activation.
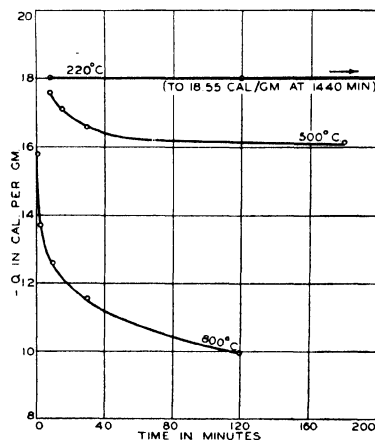
FIG. 4
Relation of Heat of Wetting to
Time of Activation.

TABLE II

Heat of Wetting and Water Content as related to Temperature and Time of Activation

Temp. °C.	Time	Water %	$-Q_w$ cal./gm.
220*	24 hrs.	3.18	18.55
220	8 min.	3.40	18.02
235	120 ”	———	18.02
500	8 ”	2.70	17.59
500	15 ”	2.43	17.11
500	30 ”	2.32	16.60
500	180 ”	2.22	16.16
800	1 ”	2.54	15.80
800	2.5 ”	1.50	13.72
800	10 ”	1.02	12.60
800	30 ”	.89	11.55
800	120 ”	.83	9.97

* Under high vacuum.

Finally, a series of measurements was made at constant time of activation (2 hours) varying the temperature and again measuring both the water content and heat of wetting. The results are collected in Table III and plotted in Figs 5 and 6.

TABLE III

Heat of Wetting and Water Content as related to Temperature of Activation

Temp. °C.	Time min.	Water %	$-Q_w$ cal./gm.
140	120	3.62	17.58
235	120	——	18.02
310	120	3.12	18.23
425	120	2.54	17.46
500	120	2.24*	16.18*
620	120	1.54	15.02
750	120	——	11.59
800	120	.83	9.97

*Values interpolated from Figs. 3 and 4.
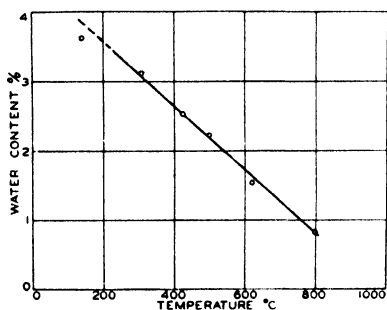
FIG. 5

Relation of Water Content to Temperature of Activation (Time of Activation = 2 hours.)
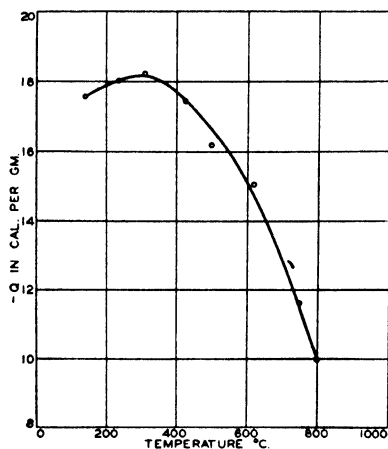
FIG. 6

Relation of Heat of Wetting to Temperature of Activation (Time of Activation = 2 hours.)

Discussion of Results

Reproducibility of Activation. The foregoing data indicate that in order to activate silica gel reproducibly, the attendant conditions must be carefully regulated. For the particular gel used in our experiments the maximum activity was obtained by heating at approximately 300° C. for a period of two hours. The activity of the product was found to be dependent upon the temperature of activation but at the lower temperatures (up to about 500°C.) the time length of treatment was of minor importance. It was also found that for at least one temperature (220°C.) the activity is not affected appreciably by heating for as long as twenty-four hours under pressure which was for periods of time as low as 5 mμ and at no time was allowed to rise above one mm. of mercury.

At high temperatures the time factor in activation becomes of nearly equal importance with the temperature factor. Thus, at 800°C. the heat of

wetting per gram was lowered more than 1.5 calories when the time of activation was increased from 30 minutes to two hours. At 500°C., on the other hand, the decrease in heat of wetting per gram was only 0.4 calories when the time of activation was increased from 30 minutes to three hours. With constant time of heating, as for example a two hour period, the drop in the value of heat of wetting for a given difference in temperature of activation was much greater in the high temperature range than in the lower. Thus, between the temperatures of 750°C. and 800°C. the decrease in heat of wetting per gram was over 1.5 calories for this 50 degree change in activation temperature, while between 310°C. and 425°C. the heat of wetting was lowered less than 0.9 calories per gram for the 115 degree change in activation temperature.

In order to activate successive samples of a given gel to the same degree, the activation temperature should be kept rather low and regulated to within about 10 degrees. The time of heating should be not less than 30 minutes, in order to insure heating the sample to the same temperature throughout. The heating may be prolonged beyond this minimum time limit but no gain in the activity of the product will result. This fact makes it unnecessary to exercise special care to heat for a definite time interval.

FIG. 7

Relation of Heat of Wetting
to Water Content.

Water in Activated Silica. It must be kept in mind that when we speak of dehydrating or of sintering silica gel to produce activated silica that we do not mean complete dehydration. Adsorptive silica appears always to contain some water, and it is with the relation of this water to activity and the manner of its retention by the gel that the remainder of this discussion will be concerned. A consideration of Fig. 7 makes immediately obvious the fact that the water content alone will not determine the activity of a gel even though the various samples are all taken from the same initial preparation. The temperature and time of dehydration are factors of equal importance with water content in determining activity. Were one to compare samples of activated silica from gels prepared in entirely different manners the divergence from a simple relationship between water content and heat of wetting would be even more striking. If the discussion be limited to a single preparation of gel such as was used in obtaining the data plotted in Fig. 7 it is seen that only one limiting condition need be imposed upon the activation treatment in order to obtain a definite relation between water content and heat of wetting. For example if it be specified that the dehydration shall be carried out in a furnace that is kept at 800°C. the relation between water content and heat of wetting, $-Q$, is shown by the plot given by the points x x x; when the de-

hydration temperature is 500°C. the short curve through the points □ □ □ is obtained. If it is specified that the time of activation of each sample be two hours, differences in water content being obtained by varying the temperature, the points on the water content-heat of wetting curve fall as indicated by the markings ○ ○ ○ and the curve is the broken line passing through a maximum at approximately 3.25% water. Though it seems necessary that an activated gel contain water, the water content is not solely the determining factor of activity. At low temperatures of activation it is found that the activity increases with a decreasing water content. At high temperatures the activity decreases with decreasing water content. At 800°C. it was found that the activity decreased markedly when the time of heating was prolonged while the water content remained practically constant.

There are still several unanswered questions concerning the water which is bound in silica gel. We have seen that it is not related in a simple fashion to the activity of the product. Why, then, cannot the water be removed without greatly reducing the activity? Is the water present because the gel is active or is the gel active because the water is present? What manner of forces are responsible for the retention of the water in the gel? The data shown graphically in Figs. 3 to 7 will help us at least partially to answer these questions.

To simplify the problem let us consider that the water retained in silica gel is held in two different ways. Consider firstly that portion of the water which is easily removed. It is found that when this water is removed in successive steps the heat of wetting of the resulting gel increases. It can quite safely be assumed that this is capillarily held water and that, by driving it out, the exposed surface of the silica becomes much greater. The vapor pressure of the water in very fine pores decreases rapidly as the radii of the pores decrease. At any given temperature, all the capillary spaces with effective radii above a certain minimum size will be swept free of water.

Consider secondly that water which is not easily removed. This water we shall designate as "bound" water. Much of this water persists within the gel at temperatures well above the critical temperature of water and, instead of being able to increase the apparent surface of the gel by its removal, we find that the heat of wetting decreases rapidly as this water is driven out. It is with the forces holding this bound water in the gel that we are immediately concerned.

We can at once rule out the theory of an adsorbed continuous film over the surface of the solid. In the first place the amount of water present in the gel is insufficient to produce even a monomolecular layer over a surface as great as we know is exposed by the silica. In the second place it is believed that removal of such a layer of water should tend to increase the heat of wetting when the solid, with its now unsaturated adsorptive forces, is immersed in water. We find experimentally, however, that the heat of wetting is decreased.

This decrease in activity is frequently explained as being due to "incipient fusion" of the solid particles with a resultant decrease in the surface area.

By "incipient fusion" is meant a partial fusion at temperatures below the normal melting point, made possible by the fact that the melting point of small particles is lower than that of large ones. It is scarcely credible that such an explanation (when referred to fusion in the sense in which this term is generally used) is sufficiently complete in the light of the fact that the decrease in activity is apparent in samples that have not been heated above 400° C.—more than 1000° below the normal melting point of the solid.

The fact that the water content-temperature of activation curve (Fig. 5) shows no irregularity at the point corresponding to the inversion point of the heat of wetting-temperature of activation curve (Fig. 6) would indicate that there is no difference in kind between the forces holding the bound water and those holding the easily removed water. There is, however, one objection to such a view. If the bound water is simply held by capillary forces in extraordinarily fine pores, one should expect that, once it is removed by vigorous activation treatment, these same pores would be refilled with the evolution of heat when the solid is immersed in water. It is evident that if we are to think of the bound water as held in capillary tubes, these tubes must, for some reason, collapse when the water is removed.

Were we to think of the bound water as forming, in some manner, part of the interlacing mass of threads the above objection would be overcome. The water molecules, forming connecting links between solid particles of silica would not have the properties of liquid water but would behave more like a solid. Hence, one might account for the stability of this water at temperatures above the critical temperature of water. On the other hand such links would constitute the weak points in the gel framework and when the temperature was elevated sufficiently these connecting water molecules would be driven out and the structure either would collapse or the adjacent silica particles would cohere. This would explain the decrease in internal surface with the removal of water at temperatures far below those at which we could reasonably expect fusion of fine particles of silica. It is significant that in the temperature range where this type of dehydration first begins (between 300°C. and 500°C.) the activity decreases very little with prolonged heating just as does the water content (Figs. 3 and 4). At higher temperatures (e.g. 800°C.) the activity continues to decrease with time of heating although the water content quickly attains a definite value which remains practically constant. This can be explained by assuming that the smallest particles of solid silica have acquired sufficient mobility at that temperature to undergo aggregate crystallization or rearrangement so as to fill or block off part of the capillary spaces, thus rather rapidly cutting down the effective internal surface area.

The theories that water is held structurally and that water is held by capillary forces, which theories have been offered as explanations of the retention of bound water, may be shown to be not very different if there is kept in mind the one essential fact that in extremely minute capillary spaces the usual laws of capillarity lose their validity. In larger capillary tubes the nature of the wall material does not enter into the computation of the capillary forces. For example, the height to which a liquid will rise in such a tube depends only

upon the radius of the capillary and is the same, whether the tube be of pyrex, quartz, soft glass, lead glass, or other material, so long as the liquid wets the wall material completely (i.e. forms a zero contact angle). In pores approximating molecular dimensions the properties of the wall exert a considerable influence on the behavior of a liquid within the pores. Terzaghi[1] has pointed out this fact in connection with his work on the plasticity of clays. When a liquid is held between solid particles that are only a few molecular diameters apart, he contends that it is in a "zone of forced vibrations." Under such conditions the liquid molecules lose much of their freedom of kinetic motion and assume more nearly the amplitude and frequency of vibration of the molecules forming the walls. When a silica gel is freshly formed there must be many points at which particles of solid come in contact. Near each point of contact there may be a region in which the solid walls are so close together that the water between them is in a "zone of forced vibrations." At greater distances from the points of actual contact between solid particles, the spaces are large enough to exhibit the usual capillary effects.

In the initial stages of drying it is the water in the larger capillary spaces that escapes and there is no noticeable change in the amount held in the so-called "zones of forced vibrations." As the gel shrinks on drying, the number of these smallest capillary spaces probably increases somewhat but the only change noticed is the decrease in effective internal volume. The final dried product, before activation, would consist then of solid silica particles holding very firmly a small amount of water which may be thought of either as structurally bound in the framework or as held in such fine capillary spaces that it is practically "solid water" and, in addition, some water filling the larger capillary spaces, held there by the forces ordinarily accompanying capillary condensation. Gentle activation treatment drives out this water, increasing the internal volume and internal surface area of the sample. When the bound water is removed, however, the surfaces of the solid particles are so close together that the surface forces which originally operated as forces of adhesion, holding water molecules in the pores, now function as forces of cohesion which tend to pull the walls of the capillaries together and thus to decrease the internal volume of the gel. Finally, at very high temperatures, aggregate crystallization occurs so rapidly that the gel loses its activity when held at such temperatures even though no water actually escapes from the gel mass.

It should be kept in mind that all silica gels are unstable and that all the changes mentioned above should occur, even tho slowly, at all temperatures. For example, it is known that over a period of years the activity of a gel decreases, even at room temperatures. This is probably due to this same phenomenon of aggregate crystallization which is speeded up at high temperatures until it becomes the predominating effect. It is our view then that in the lowest temperature range of activation the principal effect noticed is the sweeping out of capillary spaces with an attendant increase in internal sur-

[1] Terzaghi: J. Rheol., 2, 253 (1931).

face area. At somewhat higher temperatures the collapse of the gel structure due to the removal of "bound" water is the most noticeable effect. Finally, at much higher temperatures, the effects of aggregate crystallization are predominant. The absence of any sharp breaks in the curves (Figs. 3 to 7) is evidence that the change from one effect to the other is gradual as the temperature of activation is raised and therefore that there is no definite temperature at which one influence ceases to operate and another begins. There is merely a change in the relative effectiveness of the three influences as the temperature of activation is changed.

Summary

1. A brief review is given of the literature relating to the structure of activated silica gel, its water content and the temperature of activation. The theories bearing upon these topics are conflicting.

2. Using the heats of wetting by water as a measure of activity, the conditions under which silica may be activated reproducibly were determined. It was found that the activation temperature must be carefully controlled if successive portions of the gel are to be activated to the same extent.

For maximum activity this temperature should be in the neighborhood of 300°C. The length of time of heating is immaterial provided a minimum of thirty minutes is observed. Reducing the pressure while heating seems to have no appreciable effect.

3. The inter-relation of water content, heat of wetting (activity), temperature of activation, and time of activation were studied. From the results certain conclusions concerning the structure of activated silica, especially with reference to its water content, were drawn. It was shown that the water present in a gel before activation is not all held in the same manner. Part of it is held in comparatively large capillary spaces. This part is removed easily by gentle activation treatment and the activity of the silica is thereby increased. The remainder is held much more firmly, apparently in such fine capillary spaces that the retaining forces are those of adhesion rather than those of cohesion. When this water is removed from the gel, the gel structure seems to partially collapse, decreasing the internal volume (i.e. the effective surface) and the activity.

4. It is believed that at very high temperatures aggregate crystallization occurs, thus greatly decreasing the activity of the gel.

University of Michigan,
Ann Arbor, Michigan.

DYEING WITH ALIZARIN LAKE*

BY J. W. ACKERMAN

Parks[1] devised a short process for Turkey-Red Dyeing, which consisted of the preparation of a colloidal solution of alumina and soap, fixing such a colloid on the fiber, and then dyeing the mordant. The mordant adsorbs the dye, and we have a lake formed on the fiber.

Since wool will adsorb alumina, it will probably adsorb alumina with the dyestuff adsorbed on it. If this can be accomplished, it would make the process of dyeing with the mordant dyes easier and faster. It would eliminate the long and costly operations that are used to put the dyes on the fiber, for it would do away with the mordanting of wool, and the other long operations necessary to fix the dye on the fiber. With such a new method, there would be only two operations—first, the formation of the lake, and second, the adsorption of the lake by the fiber. Furthermore, the lake maker who is familiar with the formation of lakes, may prepare the lake, and the dyer would have only to run the operation of putting it in a bath and having the wool or cotton adsorb it.

A study of the problem from the standpoint of the above mentioned theory involves the consideration of three different things.

(1) Formation of the lake

(2) Peptization of the lake

(3) Dyeing with the lake

Procedure and Experimental Results

Preparation of the alumina.—Alumina may be prepared in many ways, but we eliminate the use of alum or aluminum sulphate, for Bancroft[2] has shown that the sulphate coagulates the hydrolyzed salt so readily that large amounts of alumina or basic salt are precipitated in the bath or in the fiber in such a form that it readily rubs off. The alumina was prepared by using 12.5 grams of aluminum chloride (hydr. cryst.-Kahlbaum) dissolved in 500 cc. of hot water. An electric stirrer was adjusted to stir the solution, and to the aluminum chloride was added 35 cc. of concentrated ammonium hydroxide. The alumina was immediately formed as a white gel, and was stirred for about fifteen minutes to insure complete mixing of the constituents. The alumina settled out with a clear supernatant liquid above. The alumina is positively charged, but due to its great adsorbing power it adsorbs chloride ions from the solution and the latter tend to coagulate the alumina. It was then washed

[1] J. Phys. Chem., 35, 488 (1931).

[2] Bancroft: J. Phys. Chem., 26, 515 (1922).

five times and at the last washing, it did not settle out. The washing helps remove some of the chloride ions and thus keep the alumina in colloidal solution. It was peptized completely with a small amount of HCl, which gave it a positive charge due to the preferential adsorption of hydrogen ion. It was examined in a slit ultramicroscope (Zeiss), and found to be colloidal with a slight tendency to flocculate. It was necessary to determine the amount of Al_2O_3 present, so 50 cc. of alumina were evaporated to dryness and weighed. The weights were as follows on three runs:

Run 1.—0.1262 gms.
Run 2.—0.1244 gms.
Run 3 —0.1259 gms.
Average = 0.1255 gms.

The reaction may be expressed as follows:—

$$2 \; AlCl_3 + 6 \; NH_4OH \longrightarrow Al_2O_3 + 6 \; NH_4Cl + 3 \; H_2O.$$
$$Al_2O_3 + 3 \; H_2O \longrightarrow Al_2O_3 . x \; H_2O \; (Alumina).$$
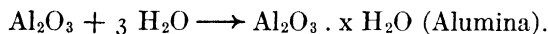
The formula is given as above, for the water content may be variable. "Since a colloidal solution is one in which a finely divided phase is kept from coalescing in some way, it is clear that there may be any number of colloidal aluminas, for instance varying from anhydrous alumina, Al_2O_3, up to the most highly hydrous form that can be obtained."[1] Bancroft has shown that this is a hydrous oxide and not a basic salt.[2]

A sodium alizarate solution was made by dissolving 2.88 gms. of alizarin (Kahlbaum) in the proper amount of sodium hydroxide and boiled to put in solution. It was diluted with water to one liter, and had a purple color. The alizarin was not used as such for it is insoluble in cold and very slightly soluble in boiling water, but dissolves readily in caustic soda. It is in true solution, as the diffusion experiments of Bull and Adams[3] have shown.

A solution of calcium acetate (0.1 N) was prepared.

Formation of the lake.—Weiser and Porter[4] have shown that the formation of the alizarin lakes from sodium alizarate baths is due to the adsorption of the dye anion, and the effect of the calcium ion on the formation of the lakes is to increase the charge on the mordant, thereby enabling it to adsorb more of the dye anion. Also they have shown that the effect of the calcium is marked and increases with its concentration.

"By the addition of a strongly adsorbed cation one may use a slightly basic bath in which the alizarin is soluble and at the same time avoid the displacement of the dye anion by the OH. That the effectiveness of the calcium is not due to the direct precipitation of the calcium alizarate is evidenced by the fact that the quantity of calcium present may be greater than the equivalent of the alizarin without the dyebath becoming exhausted."

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[1] Bancroft: "Applied Colloid Chemistry," 204 (1926).

[2] Bancroft: J. Phys. Chem., **18**, 435 (1914).

[3] Bull and Adams: J. Phys. Chem., **25**, 660 (1921).

[4] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927); Weiser: J. Phys. Chem., **33**, 1713 (1929).

It was thought best to check this work, since it was suggested by Bull and Adams,[1] and Williamson[2] that the formation of the alizarin lakes is due to the direct adsorption of the neutral sodium alizarate.

Alizarin forms a purple solution when dissolved in alkali, and a thin film of sodium alizarate is purple both in transmitted and reflected light. Alizarin acid is insoluble in water, and the alcoholic solution has a reddish-yellow color similar to that of the solid crystals. If neutral, undissociated sodium alizarate was taken up by the alumina, we should expect the lake to be colored purple.

Experiments were run with alumina and sodium alizarate in varying proportions, and in no case was there a purple lake formed. The alumina was made from aluminum chloride and ammonium hydroxide, and since there are probably chlorine ions present, the next experiments were run with a pure alumina, made according to a method given by Mellor.[3]

"If a clean strip of aluminum be placed in a bottle containing a few cc. of mercury and all shaken, the aluminum when exposed to air, rapidly oxidizes, and white tufts of alumina grow up to about a cm. above the surface of the metal. If the aluminum be placed in water instead of in air, the water is decomposed, and the aluminum oxidized. If a little mercury be poured into a beaker of water and a clean strip of aluminum be dipped in the vessel, no action occurs until the aluminum touches the mercury. The water then decomposes and the action continues until all the aluminum has been transformed into alumina, and this even after the mercury has been removed."

An alumina was made according to this method, and then treated with sodium alizarate. In no case was a purple lake formed, and a red lake resulted due to the adsorption of the alizarin anion.

In order to show that the solid sodium alizarate is purple, drops of the sodium alizarate solution were placed on a porous white plate, and the concentrations were varied from very weak to very concentrated. For each drop the color was purple. Also a solution of sodium alizarate was evaporated to dryness on a water bath, and the color was purple. However, it must be kept in mind that in dilute solutions the color is red.

The color then is not due to sodium alizarate, but probably due to the alizarate anion. This was shown by preparing the pure alumina and treating it with alizarin in solution, which is prepared by dissolving the crystals of alizarin in alcohol and heating to get in solution. The alizarin was used in varying concentrations, and it was found that a series of lakes were formed varying from a pink color to a red. Following a suggestion of Weiser the newly formed oxide was suspended in alcohol and treated with an alcoholic solution of alizarin. In this way the precipitation of the alizarin is prevented. A red lake was formed similar to that obtained with sodium alizarate.

Since the color of the lake with sodium alizarate is red and not purple, as it should be if neutral sodium alizarate was taken up, nor the orange of the

[1] Bull and Adams: J. Phys. Chem., 25, 660 (1921).

[2] F. S. Williamson: J. Phys. Chem., 28, 891 (1924).

[3] J. W. Mellor: "Modern Inorganic Chemistry," 774, (1925).

alizarin acid, and since the color of the lake is red when pure alumina is treated with alizarin acid we conclude that the color of the lake is due to the adsorption of the alizarate anion by the alumina.

This confirms the results of Weiser.[1] "The color of the alumina-alizarin lake is neither the dark purple to purplish black of thin films of alkali and alkaline earth alizarates nor the yellow orange of the alizarin acid, but is a bright red suggestive of the color of alizarate ion in aqueous solution.

"A newly formed oxide free from adsorbed ions will form a red lake either from an aqueous solution of sodium alizarate or from an alcoholic solution of alizarin. Depending on the conditions of formation and the age of the oxide, the adsorption of alizarate may be exchange adsorption, direct adsorption, or both.

The effect of calcium was tested by adding a solution of calcium chloride to a solution of sodium alizarate in varying concentrations, and in every case a purple precipitate was formed. When insufficient calcium is added a purple precipitate is obtained and a red filtrate, which is probably sodium alizarate. Some of this filtrate was added to alumina and a red lake was produced which did not change its appearance when treated with more calcium. Also to the alcoholic solution of alizarin calcium chloride was added and a brown precipitate and some purple precipitate were formed. The former is due to the alizarin precipitating and the latter is due to the formation of calcium alizarate. Since the color of calcium alizarate is purple, and since calcium added to an alumina lake does not produce a color lake but intensifies the red color, the conclusion of Weiser that the effect of the calcium ion is to increase the charge on the mordant, thereby enabling it to adsorb more of the dye anion, is the correct one.

The lake is then formed by the addition of sodium alizarate to alumina, and then the addition of calcium acetate.

The lake was made as follows:—

200 cc. of alumina
75 cc. of sodium alizarate was added
25 cc. of calcium acetate (0.01 N) was then added

Temperatures: Room Temp. (25°), 30°, 35°, 45°, 55°, 65°, 75° and 85°.

A red lake was formed in all cases, which settled out on standing. The lake at 25° was chosen for peptization experiments, for Bancroft[2] has shown that the amount of adsorption must decrease with rising temperature, and this lake would contain the greatest quantity of the dye adsorbed.

Peptization of the lake.—Since the lake settled out on standing it would be better to peptize it, for then it would be in colloidal solution and taken up more readily by the fiber.

With ammonium hydroxide:—Weber[3] said that the solubility in dilute ammonia is a property common to all the alumina lakes of the ortho-dihy-

[1] Weiser: J. Phys. Chem., **33**, 1713 (1929).
[2] Bancroft: "Applied Colloid Chemistry," 131 (1926).
[3] Weber: J. Soc. Chem. Ind., **12**, 650 (1893).

droxyl dyes. Alizarin is the classical ortho-dihydroxyl dye, so Weber's statement suggested that the lake might be peptized by using ammonium hydroxide.

Peptization with ammonium hydroxide.—A dilute solution of ammonium hydroxide was made by adding 500 cc. of water to 100 cc. of concentrated ammonium hydroxide. The lake was made as before, but no calcium was added. Using a constant amount of lake, the following amounts of ammonium hydroxide were added, after the lake had settled out.

Amount of Lake	Amount of NH₄OH	Temp.	Result		
15 cc.	1 cc.	Room	Lake precipitated out		
,,	2 cc.	,,	,,	,,	,,
,,	3 cc.	,,	,,	·,	,,
,,	4 cc.	,,	,,	,,	,·
,,	5 cc.	,,	,,	,,	,,
,,	10 cc.	,,	,,	,,	,,
,,	15 cc.	,	,	,,	,,
,,	20 cc.	,,	,,	,,	,,
,,	25 cc.	,·	,,	,,	,,
,,	30 cc.	,,	,,	,,	·,
,,	35 cc.	,,	,,	,,	,,
,,	40 cc.	,,	,,	,,	,,
,,	45 cc.	,,	,,	,,	,,

The same runs were made at the following temperatures: 30° C, 35°, 40°, 45°, 50°, 55°, 60°, and 65°. Result: These lakes were all precipitated out.

The lake is precipitated before the addition of the ammonium hydroxide by the sodium alizarate and the addition of the hydroxide only increases the negative charge on the particles and thus keeps them precipitated instead of peptizing them.

The lake was made according to the formula previously given with the calcium acetate present. The same amount of lake and the same amounts of dilute ammonium hydroxide were used with the temperature varied as in the previous attempt for peptization.

The results were the same as before—the lake precipitated out. The conclusion is then drawn that ammonium hydroxide will not peptize the lake under the conditions given.

A better method to peptize the lake would be to add the ammonium hydroxide and then the sodium alizarate. In this way, the alumina would probably be peptized and also the lake. This experiment was not carried out, for a subsequent experiment showed that the addition of a peptizing agent is unnecessary.

Peptization of alumina with acetic acid.—The peptization of alumina by acetic acid was done by Bentley and Rose,[1] although they claimed that a

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[1] Bentley and Rose: J. Am. Chem. Soc., **35**, 1490 (1913).

colloidal basic acetate was formed and not colloidal alumina. K. C. Sen[1] was able to peptize alumina with acetic acid.

Following the outline of Sen's work it was found that alumina could be peptized by acetic acid, but that the amount of acid reaches a maximum. With increase in concentration the stability decreases which is probably due to the fact that since the suspension is positively charged, the increasing concentration of the negative ion of the acid will have a coagulating effect on it.

The alumina was made as before from aluminum chloride and ammonium hydroxide. The acetic acid used was 8% and at a temperature of $60°$ C.

Run	Amount of alumina	cc. Acetic acid added	Result
1	25 cc.	1 cc.	Peptized
2	25 cc.	2 cc.	''
3	25 cc.	3 cc.	''
4	25 cc.	4 cc.	''
5	25 cc.	5 cc.	Small amount settled out
6	25 cc.	6 cc.	More than Run 5 settled out
7	25 cc.	7 cc.	'' '' '' 6 '' ''
8	25 cc.	8 cc.	Almost completely ppt.
9	25 cc.	9 cc.	Precipitated out

This checks the results of Sen.

Peptization of the lake with acetic acid.—Since it is possible to peptize alumina, the next experiment is to try to peptize the alumina when the alizarate anion is adsorbed. The general scheme was to take a constant amount of lake and add to it varying amounts of acetic acid, keeping the temperature constant, and the strength of the acetic acid constant.

The amount of lake was 15 cc., the temperature was $25°$ C. and the cc. of acid used were 1, 2, 3, 4, 5, 10 and 25 cc. The concentration was 1%. The result was that the lake precipitated out.

Then keeping the amount of lake constant as before, the same acid was varied from 1% to 15%. The lake precipitated as before.

Finally, the same runs were made as the following temperatures: $45°$, $55°$, $65°$ and $75°$ C. The results were the same—the lake precipitated out.

The conclusion is that dilute acetic acid will not peptize the lake through the range of temperatures given. Weiser[2] has shown by cataphoresis experiments that the lake is negatively charged. The addition of hydrogen ions from the acetic acid will tend to neutralize the charge on the lake, and it would be precipitated and not peptized.

Peptization of the lake without the addition of outside peptizing agents.— Weiser and Porter[2] found that the proper amount of sodium alizarate would peptize the lake. This is the best way to peptize the lake for it eliminates the addition of a peptizing agent.

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[1] K. C. Sen: J. Phys. Chem., **28**, 1029 (1924).
[2] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927).

The general scheme was as follows:—

The runs were carried out at room temperature. 5 cc. of sodium alizarate was placed in a 100 cc. glass stoppered bottle. 25 cc. of alumina was added and the bottle shaken immediately. Results: Temp. = Room temperature (25° C.)

Run	cc. Alumina	cc. Na Alizarate	Color	Result
1	25	5	Orange	Lake precipitated out
2	25	10	Deep red	,, ,, ,,
3	25	11	,, ,,	,, ,, ,,
4	25	12	,, ,,	Lake settled out slightly
5	25	13	Red	,, ,, ,, ,,
6	25	14	,,	Lake stayed in suspension
7	25	15	,,	,, , ,, ,,
8	25	16	,,	,, ,. ,, ,,
9	25	17	,,	,, ,, ,, ,,
10	25	18	,,	,, ,, ,, ,,
11	25	19	,,	,, ,, ,, ,,
12	25	20	,,	,, ,, ,, ,,
13	25	21	Red-violet	After standing a small quantity settled to the bottom
14	25	22	,, ,,	Same as previous run but a little more settled out
15	25	23	,, ,,	Same as previous run but more settled out
16	25	24	Violet-red	Settled out
17	25	25	Violet	,, ,,
18	25	30	,,	,, ,,

Color—There is a gradual increase in the red color until run No. 13 where it goes toward the violet and then keeps increasing in violet color through run No. 18.

In the runs 1-3, the adsorption of the dye anions which are negatively charged neutralize the positive charges on the alumina, so that the lake settles out. The precipitation is less marked in runs 4 and 5, and between runs 5 and 6, which is a difference of 1 cc. of sodium alizarate the lake or the alumina reaches the iso-electric point, and with 14 cc. of sodium alizarate the alumina becomes negatively charged and stays in suspension. The addition of more of the sodium alizarate did not have any apparent effect until the total quantity present was 21 cc. More than this started precipitation and when 25 cc. had been added the precipitation was complete.

The lake in suspension was examined with a slit ultramicroscope (Zeiss) and exhibited colloidal particles, uniformly dispersed, in lively Brownian movement.

Peptization of the lake (calcium added).—We have said that the effect of the calcium ion on the formation of alizarin lakes is to increase the charge on

the mordant, thereby enabling it to adsorb more of the dye anion. It was thought advisable to work on the lake with calcium acetate added, because more of the dye anion is adsorbed.

The lake as made in the previous run No. 7 was used, because it was of good color and stayed up in suspension. A solution of 0.01 N calcium acetate was used.

The general run was as follows: 15 cc. of sodium alizarate was placed in a glass stoppered bottle (100 cc.); added 1 cc. of calcium acetate and then 25 cc. of alumina. The bottle was shaken, and a red lake was formed.

The runs were made at room temperature. The amount of sodium alizarate used in each run was 15 cc., the amount of alumina used was 25 cc., and the calcium acetate was varied.

Run	Calcium Acetate	Color	Result
1	1 cc.	Deep red	Lake stayed in suspension
2	2 cc.	" "	" " " "
3	3 cc.	" "	" " " "
4	4 cc.	" "	Settled out slightly
5	5 cc.	" "	Settled more
6	6 cc.	" "	Settled more than run No. 5
7	7 cc.	" "	" " " " " 6
8	8 cc.	" "	Almost completely ppt.
9	9 cc.	" "	Precipitated out

The lakes in suspension were examined with an ultramicroscope and exhibited colloidal particles clustered together in loose aggregates (10 to 30 particles in an aggregate), but with only slight Brownian movement within the clusters, which indicated a tendency to flocculate.

The calcium added in runs 1-3 is adsorbed by the alumina and increases the positive charge on the mordant, thereby enabling it to adsorb more of the dye anion. There is not enough adsorbed to precipitate the lake, so it stays in suspension. As the concentration of the calcium is increased, its effectiveness increases and more dye anions are taken up by the alumina. However, a point is reached at which the adsorption of more dye anions is the same as adding more sodium alizarate. As in the case of the lake made with the alumina and sodium alizarate, a point is reached at which the addition of more dye anions starts the precipitation of the lake. This starts at run No. 4 and the lake precipitates more and more until at run No. 9 it is precipitated completely.

The lake will then remain peptized as long as the calcium acetate is not added to the point at which it starts the precipitation of the lake. This lake can then be used for dyeing, since it is peptized.

Dyeing wool with alizarin lake:—A ball of wool (Fleisher's Knitting Worsted) was cut up into strips about two feet long.

The yarn was first (washing the wool) treated with a warm, dilute solution of Ivory soap and was then rinsed in tap water followed by many changes of hot distilled water.

The yarn was dried under a bell jar which contained some calcium chloride to take up the moisture.

The lake for use in the dyeing was made as follows:

> 75 cc. of sodium alizarate
> Add 15 cc. of calcium acetate —0.01 N
> Then add 175 cc. of alumina

This was carried out at room temperature and the lake was stirred with an electric stirrer for a half hour, to insure complete mixing.

Run No. 1—The lake was put in a 500 cc. R.B. flask with a condenser attached to prevent evaporation. A sample of the fiber weight 1.27 gms. was put into the bath after it had been brought to a boil. Then slow but steady boiling was continued for forty-five minutes. The fiber was removed and allowed to stand under the bell jar with calcium chloride in it. The following day it was dry and found to weigh 1.29 gms. The wool was colored a deep red color. The sample of the fiber was tested by boiling in distilled water for a half hour. The water was colored and the lake was taken off the fiber to a large extent.

Run No. 2—The same procedure was followed as in Run No. 1, but the bath was boiled for two hours with the fiber in it, and the rate of boiling was kept the same as No. 1 by estimation of the size of the flame and the rate of condensing. In this run the weight was found to be increased by 0.04 gms. The wool was dyed a deep red. The fiber was boiled in distilled water for one half hour, and part of the color came out of the fiber, but not as much as in run No. 1.

Run No. 3.—The same procedure was followed as in Run No. 1, but the bath was boiled for three hours with the fiber in it. In this run the weight of the fiber was found to be increased by 0.06 gms. After drying the wool was dyed a deep red. The fiber was placed in boiling distilled water for one half hour and the water was slightly colored, but very little color came off the fiber.

Run No. 4.—The same procedure was followed as in Run No. 1, but the bath was boiled for four hours with the fiber in it. In this run the fiber was found to have increased 0.068 gms. in weight. The wool was dyed a deep red. The fiber was placed in boiling distilled water for one half hour and the water was colorless.

Tests on the Dyed Fibers

Fading.—The tests for fading were carried out by means of the Fade-ometer. The particular "Color Fade-ometer" used was run so that twenty hours of exposure to the Fade-ometer was equivalent to fifty hours of direct June sunlight.

The fibers were exposed for a total of eighty hours, equivalent to two hundred hours of sunlight.

Results.—Sample 1.—This was faded very little, but it was noticed that it had an appearance of being a little more yellow than the original sample. The fading is so slight that it can be ignored.

Sample 2.—This was the same as Sample 1.

Samples 3 and 4.—The samples were changed a little by fading, since they had a yellow tinge. The fading is so slight that they can be considered fast to light.

Bleeding.—This has been explained under the various runs. It was noted that in run No. 4 the bleeding was negligible, so that the conclusion is that the fibers must be boiled in the bath between three and four hours. This is probably due to the fact that the longer boiling coagulates the lake on the fibers.

Action of soap.—A fairly concentrated solution of soap was made by cutting the Ivory soap and boiling in distilled water. The dyed fibers were then allowed to boil in the solution for one half hour and when removed, rinsed and dried, no change could be detected.

Action of acid.—A strip of the dyed fiber was steeped for one hour in a 5% acetic acid solution. It was removed, rinsed and dried. No change could be detected.

The wool was dyed a deep red color, and is very fast under the conditions given. There is little fading, only a slight bleeding, and the color resists the action of soap and also of acid. The color is satisfactory, but since a little color was washed off the fiber, the use of Turkey-red oil to fix the alumina more strongly on the fiber was tried. Weiser and Porter[1] say: "If the fiber is treated with so-called sulphonated oils before mordanting with alumina, there results the brilliant Turkey-red, a color remarkable for its fastness to light and the action of soap and water."

Treatment of the fiber with Turkey-red oil.—Parks[2] has shown that sulphonated oils are adsorbed by cotton. Similar experiments with wool show that it adsorbs the sulphonated oil.

The purpose of this set of experiments was to determine which was more desirable:

(1)   Fibers treated with Turkey-red oil and then dyed.

(2)   Fibers dyed and then treated with Turkey-red oil.

Run No. 1.—Wool, which had been kept under the bell jar containing calcium chloride, was dried in an oven at 50°C. for twenty-four hours. Pieces of wool were then placed in solutions of Turkey-red oil and shaken in an electric shaker for eighteen hours at room temperature. The wool was then removed from the solution and hung up to dry without previously pressing out the oil. However, the surplus could drain from the sample. After air-drying, the samples were then used for the dye bath.

A lake was made by adding 75 cc. of sodium alizarate to 200 cc. of alumina, and then adding 15 cc. of 0.01 N calcium acetate. 190 cc. of the above lake was used for the dyebath, which was brought to a boil. The wool was added and the bath was allowed to boil for four hours. Slow but steady boiling was

[1] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927).

[2] Parks: J. Phys. Chem., **35**, 488 (1931).

maintained. The wool was dried at room temperature. It was dyed a deep red color, which was uniformly fixed on the fiber, and did not rub off.

Run No. 2.—The same bath was used as in the previous run, and the wool was dyed a red color. It was then placed in a bottle containing the same concentration of Turkey-red oil and shaken for eighteen hours. It was dried at room temperature. It was noted that the excess Turkey-red oil solution was a pink color at the end of the shaking, which indicated that part of the lake came off the wool.

The result was a red of much brighter color than in the previous run. It was a brighter color for the wool had a shiny appearance, but the loss of color would not compensate for the additional brilliance of the finished product.

Run No. 3.—This experiment was made to show the relative colors of the wool impregnated with Turkey-red oil and then dyed, of wool dyed and then treated with the oil, and finally of wool dyed with no treatment of oil.

The same bath was used as in the previous runs, and the wool was used in the same amount and dyed in the same manner, without the use of Turkey-red oil. The red color obtained was lighter than Run No. 1 (wool impregnated and then dyed), but darker than Run No. 2 (wool dyed and then impregnated).

The conclusion is that for the deeper color it is better to treat the fiber with oil and then dye; and for a brighter color it is better to dye the wool and then treat with oil, although the color is less intense.

Mr. Parks[1] has found that Turkey-red oil has a great affinity for alumina and is adsorbed by the cotton. He also says: "Experiments with Turkey-red oil and soap solutions show that whenever they come in contact with aluminum salts a colloid is formed. Therefore, if sulphonated oil be adsorbed by the fiber and this brought in contact with a bath of aluminum acetate, a colloid is formed which is fixed on the fiber. And since experiment shows that alumina removes soap from solution, the above-mentioned colloid must be due to the adsorption of alumina from solution by the sulphonated oil or soap. In fact the fiber is mordanted with alumina fixed by the oil or soap. Heat coagulates this colloid which then has the property of adsorbing more sulphonated oil or soap; and thus can adsorb more alumina. This is a property made use of by the dyers who repeat the oiling and metallic mordanting process several times in order to obtain a suitable amount of oxide on the fiber."

This explanation is applicable for our results. The wool adsorbs the Turkey-red oil, and when it comes into contact with the lake, the oil adsorbs the alumina or lake, and heat coagulates the colloid which then adsorbs more alumina and fixes it on the fiber.

Cotton Dyeing with Alizarin Lakes

Ordinary cotton cloth was used for this work, and the finish was destroyed by boiling the cloth in dilute alkali for one hour. It was then dried at room temperature.

[1] Parks: J. Phys. Chem., 35, 488 (1931).

A bath of the lake was prepared as follows:—To 200 cc. of alumina was added 75 cc. of sodium alizarate and then 15 cc. of 0.01 N calcium acetate. A red lake was formed.

The cloth strips were put in the boiling bath, and boiling was continued for four hours. The cloth was removed, washed and dried at room temperature. The color on the cloth was a good red, but a little lighter than that obtained with the wool.

The same theory applies for the dyeing the cotton as was used for the wool. Briefly, the alumina adsorbs the alizarate anion of the sodium alizarate and a red color is produced. Then the cotton cloth adsorbs the alumina and is thus dyed red.

The tests, which were used for the dyed wool were applied to the dyed cotton, except the fading test, which was omitted for lack of time. However, we may assume that approximately the same amount of fading would take place on the cotton as on the wool.

Bleeding.—The cloth was boiled in water for one half hour and very little color came off the fiber.

Acid.—A piece of the dyed fiber was steeped for one hour in a 5% acetic acid solution. It was removed, rinsed and dried. No change was observed in the color.

Soap.—A fairly concentrated solution of soap was made by cutting up Ivory soap and boiling in distilled water. The dyed fibers were then allowed to boil in the solution for one half hour, and when removed, rinsed and dried, no change could be detected.

Form to send out the lakes.—The lake may be sent out in the form of a paste. When the lake has been nearly filtered dry, it may be taken from the filter, mixed thoroughly with the small amount of water left, placed in bottles and shipped from the lake maker to the dyer. The paste then is redissolved in the required amount of hot water and is ready for use. The disadvantage of this method is that the lake must be shipped in bottles or some other container, which will prevent the evaporation of the water.

Another method was tried in which a dilute solution of sodium oleate was added to the lake. Sodium oleate is a water-soluble colloid and is peptized by water. Therefore, if the lake takes up the sodium oleate and is then dried, the sodium oleate will carry the particles of the lake into suspension, when it is redissolved in water. After the addition of the sodium oleate, the lake was dried, then dissolved in water again, and then the dyeing operation was carried out. However, the wool when dyed and dried pulled apart due to the alkali in the lake from the sodium. This was remedied by treating the lake with dilute acetic acid before dyeing, which will neutralize the alkali formed. The wool was then dyed again and this method was found to be satisfactory. The lake might be treated with a dilute solution of ammonium oleate, which would not form an alkali strong enough to attack the wool, and which consequently would make the addition of acetic acid unnecessary.

Formation of a red lake from calcium phosphate and alizarin.—Another method for the preparation of a red lake was suggested by an observation of

Edward Bancroft:[1] "The remarkable effect of madder in giving its red colour to the bones, but not to the soft parts of animals, with whose food it had been mixed appeared to indicate a considerable attraction between the calcareous earth and the coloring matter of this root, and I was induced by it to employ the former as a basis for the latter, in dyeing on both wool and cotton; but the effect did not answer my expectations, as neither lime recently burnt, nor the carbonate of it, when mixed with madder in water, produced colours more lively and permanent than madder alone. But broadcloth, boiled in water with lime and sulphuric acid, in such proportions as to neutralize the latter; and afterwards dyed with madder took a lasting red colour, though not so bright as when dyed upon the aluminous basis. Cotton, however, being treated in the same manner, was but slightly discolored.

"Mr. John Belcher by adding some powder of madder roots to the food of dunghill fowls, found that a similar redness was thereby contributed to their bones; and he gave accounts of his observations and experiments to the Royal Society, which were printed in the Phil. Trans. No. 442, and No. 443, (1736)."

Since the principal constituent of bones is tricalcium phosphate, and that of madder is alizarin, it was thought that a lake might be made with the phosphate as mordant and alizarin as dyestuff.

Procedure and Experimental Results

Mordant.— Solutions for the mordant were made up of calcium chloride (Kahlbaum) of a strength—2 grams in 50 cc. of water, and normal sodium phosphate (Na_3PO_4) of a strength—1 gram in 350 cc. of water.

The mordant was made up in the following manner, using 50 cc. of calcium chloride throughout the run.

Run	cc. Na_3PO_4	Result
1	30	Flocculent white precipitate
2	25	,, ,, ,,
3	20	,, ,, ,,
4	15	,, ,, ,,
5	10	,, ,, ,,
6	5	Flocculent white precipitate
7	4	,, ,, ,,
8	3	White precipitate—Settled more than No. 7
9	2	,, ,, ,, ,, ,, ,,
10	1	,, ,, ,, ,, ,, ,,

A solution of alizarin was prepared by dissolving alizarin in a solution of water and alcohol. An orange-yellow solution was obtained.

[1] Edward Bancroft: "Philosophy of Permanent Colours," 2 (1813).

In order to determine the best lake it was necessary to add a constant amount of alizarin to the various mordants.

The experiments were done at room temperature.

Mordant or Run	cc. Alizarin	Result
1	5	Deep red flocculent ppt.
2	5	,, ,, ,, ,,
3	5	Red flocculent ppt.
4	5	,, ,, ,,
5	5	Wine red flocculent ppt.
6	5	,, ,, ,, ,,
7	5	Red flocculent ppt.
8	5	Light red flocculent ppt.
9	5	,, ,, ,, ,,
10	5	,, ,, ,, ,,

The results show that we can obtain a range in color from deep-red to light-red, and what Edward Bancroft observed was the formation of a lake between tricalcium phosphate and alizarin, and it was this lake which gave the red color to the bones.

Dyeing.—For the dyeing, a lake was made as follows:—50 cc. calcium chloride, 30 cc. of normal sodium phosphate and 15 cc. of alizarin. A red lake was obtained. It was boiled and then the wool was added. The bath was boiled for three hours, and a bright red color was produced on the wool. It was brighter and lighter than the lakes made with alumina as mordant.

Tests on the Dyed Fibers

Fading.—There was practically no fading with the use of the Fade-ometer, after an exposure of forty hours, equivalent to one hundred hours of direct sunlight.

Bleeding.—Boiling in water does not affect the color.

Acid.—Dilute sulphuric acid takes a small quantity of color off the fiber. Hydrochloric acid—destroys the color on the fiber.

Base.—Ammonium hydroxide turns the color purple.

Conclusions

The process of dyeing Turkey-red as practised may be summarized as follows:

(1)   The fiber is bleached.

(2)   Some soap-forming oil is adsorbed on the fiber.

(3)   The oil is saponified on the fiber.

(4)   The excess soap and oil is removed from the fiber.

(5)   The soap containing fiber adsorbs alumina.

(6)   The alumina adsorbs alizarin ions and calcium ions.

(7)   The clearing operations remove the dirt, increase the size of the particles, and varnish the dyed fiber with a very thin film of tin soap.

In the process for dyeing Turkey-red as proposed in this paper, a lake is made by the addition of sodium alizarate and calcium acetate to alumina. This lake can be used directly for dyeing, because the wool adsorbs the alumina, which has already taken up the dye. The lake maker can prepare varying ranges of color by different proportions of the materials, and the dyer may obtain different results by the use of Turkey-red oil before or after dyeing.

Since alizarin is the chief example of the Mordant dyes, this method of dyeing is applicable to this class. However, the possibilities have been barely touched. With additional work, we might include part of the substantive dyes—those that do not dye wool directly, and the developed dyes which are so insoluble that they do not dye in the bath. Also the methods ought to be worked out for another mordant, such as the hydrous oxide of chromium. With this mordant, chrome colors should be tried, such as Solochrome B, etc. The limitations are few for the method and any color that requires a mordant could probably be used. Many differences in shades, brilliancy and strength of color could be worked out by slight changes in the method to fit the particular dyestuff.

Summary

1. Alumina treated with a solution of sodium alizarate or with an alcoholic solution of alizarin yields a red lake.

2. The alumina adsorbs the alizarate anion, producing the red color.

3. Sodium alizarate in the solid state is purple, but in dilute solutions it is red.

4. The purpose of the calcium is to increase the amount of the alizarate anion taken up.

5. The results 1-4 confirm the work of Weiser and Porter on the alumina-alizarin lakes.

6. The lake cannot be peptized with ammonium hydroxide, under the conditions given.

7. The lake cannot be peptized with acetic acid, under the conditions given.

8. The lake is peptized by adding the proper amount of sodium alizarate to alumina.

9. A method of dyeing with alizarin lakes is described.

10. The use of Turkey-red oil with lakes is discussed.

11. A red lake is formed by the use of tricalcium phosphate and alizarin.

Acknowledgment

Cornell University.

PARTICLE SIZE AND CONSTITUTION OF COLLOIDAL FERRIC OXIDE. II. DIALYSIS AND AGING*

BY J. B. NICHOLS, E. O. KRAEMER, AND E. D. BAILEY

In continuation of the investigation of the factors influencing the particle-size distribution of hydrous ferric oxide,[1] attention has been given to the effects of dialysis and of aging.

Determination of Particle Size

The low-speed Baltic type of ultracentrifuge was used throughout this investigation.[2] All of the determinations were made at a temperature of 30° and a speed of 10,080 r.p.m., corresponding to a centrifugal force about 5,000 times that of gravity. A preliminary value of 4.5 was used for the density of the particles. This value is admittedly uncertain, and in some cases differences in the distribution curves obtained may be due to differences in particle density as well as in particle size. The question of particle density will be considered in a separate investigation. For the determination of particle-size distribution curves of the ferric oxide, the centrifugal form of Stokes' law was used.[3] The particle-size distribution curves obtained from the ultracentrifuge are designated as *weight-optical* distribution curves because in a polydisperse system of particles the light absorption may change with radius;[4] only when the absorption coefficient is independent of particle size does a weight-optical curve coincide with the weight-distribution curve.

Preparation of Sols

A stock solution of approximately two-molar ferric chloride was used for the present investigation. The ferric oxide sols were made by diluting portions of this stock to the desired concentrations and hydrolyzing at 100° under a reflux condenser to prevent the loss of water and of hydrochloric acid formed. The hydrolytic action was stopped, after drawing off the sample, by cooling rapidly to room temperature.

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[1] Nichols, Kraemer, and Bailey: J. Phys. Chem., **36**, 326 (1932).

[2] Svedberg and Heyroth: J. Am. Chem. Soc., **51**, 550 (1929).

[3] For the theory underlying the determination of distribution curves by means of the ultracentrifuge, see Svedberg and Rinde: J. Am. Chem. Soc., **46**, 2681-85 (1924); Rinde: "The Distribution of the Sizes of Particles in Gold Sols," Diss., Upsala (1928); and Svedberg: "Colloid Chemistry," 171 (1928).

[4] For a more complete discussion see Ref. 1, page 328.

Dialysis of a Fresh Sol

The fresh sols contain free hydrochloric acid and probably ferric chloride or basic chlorides in solution as is evident from the equation of the hydrolytic reaction

$$FeCl_3 + 3H_2O \leftrightarrows Fe(OH)_3 + 3\ HCl$$
$$\text{or}\quad FeCl_3 + xH_2O \leftrightarrows Fe(OH)_xCl_{3-x} + xHCl$$
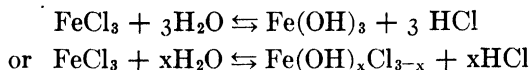
The insoluble ferric hydroxide or basic chloride initially formed immediately undergoes a process of dehydration and condensation to colloidal particles of hydrous ferric oxide. We should expect the equilibrium established at 100° to be shifted back to the left when the system is cooled down to room temperature. This shift would occur immediately with a soluble hydroxide, but when a colloidal phase is involved, as in the case under investigation, the reversal is sluggish and may never be quite complete. Ordinarily, advantage is taken of this slowness of re-solution to stabilize the sols and to reveal the properties of the colloidal system itself by eliminating the electrolytes through dialysis. Since electrolytes exert such an important influence on the stability and flocculation of colloidal systems, the elimination of the electrolytes might be expected to be accompanied by changes in the colloidal fraction. Such changes might involve further hydrolysis of ferric chloride, aggregation of primary particles, or disaggregation of secondary particles, depending on the concentration and the nature of the electrolytes. In all cases changes should be reflected in the particle-size characteristics. Accordingly, an ultracentrifugal analysis was made of sols of ferric oxide at various stages of dialysis. A one-day-old sol formed from 0.037 M FeCl₃ was used for this study.

The dialysis arrangement was similar to that used by Neidle.[1] A slow current of distilled water was allowed to flow through a collodion bag dipping into a beaker containing 800 cc. of the sol at 35°C., which was kept in constant motion past the wall of the bag by means of a Hamilton-Beach mixer. Samples were removed after 4.5, 11, 23.5, and 47.5 hours. At the end of 47.5 hours the dialysate gave no test for iron with ammonium thiocyanate solution or for chloride with silver nitrate.

TABLE I

Effect of Dialysis on Freshly Prepared Ferric Oxide from 0.037 M FeCl₃

Sol	Time of Dialysis (Hours)	Total Fe g.eq./l.	Total Cl g.eq./l.	Purity Fe/Cl	Colloidal Fe g.eq./l.	Weight-Optical Mean Radius
Fe-31	0	0.1166	0.1112	1.0	0.0900	3.8 mμ
Fe-32	4.5	0.1049	0.0464	2.3	—	4.2
BD-V	11.0	0.1039	0.0185	5.6	0.1014	—
Fe-36	23.5	0.1007	0.0047	21.6	0.0991	4.4
Fe-35	47.5	0.1039	0.0024	43.8	0.1039	4.0

[1] Neidle: J. Am. Chem. Soc., **38**, 1270 (1916).

Changes in Composition: Table I gives the compositions of the series of samples obtained. The iron analyses were made by the Knop dichromate method[1] with diphenylamine as indicator. Neither the potassium permanganate titration nor the thiocyanate colorimetric method gave reliable results with these colloidal ferric oxide samples. The purity of the sols is expressed by the ratio of equivalents of iron to equivalents of chlorine per liter. The table shows first that the stirred dialysis produced a rather rapid elimination of chlorine and that the sol reached a moderate purity in two days of dialysis. During the dialysis the sol underwent some evaporation and
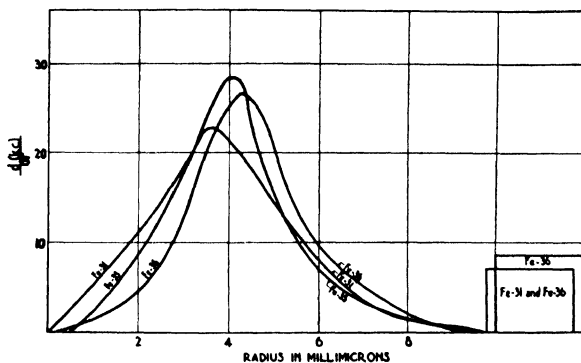
FIG. 1

EFFECT OF DIALYSIS ON THE WEIGHT-OPTICAL DISTRIBUTION CURVE OF ONE-DAY-OLD FERRIC OXIDE FROM 0.037 M FeCl$_3$

Sol	Time of Dialysis (Hours)	Primary Mean Rad.	Primary Area	Secondary Mean Rad.	Secondary Area
Fe-31	0	3.8 mμ	86%	ca. 20 mμ	14%
Fe-32*	4.5	4.2	88	ca. 20	12
Fe-36	23.5	4.4	86	ca. 20	14
Fe-35	47.5	4.0	83	ca. 20	17

*Distribution curve for Fe-32 omitted to avoid confusion of lines.

osmotic dilution. Towards the end of the dialysis, when osmotic dilution was negligible, the increase in total iron concentration was due to evaporation. The total volume of the sol recovered, including the portions removed during the dialysis was 785 cc., as compared with the starting volume of 800 cc. The total loss of ionic iron by dialysis amounted to about 13%.

Changes in Particle Size: The changes in particle size of the colloidal component during dialysis are represented by the distribution curves of Fig. 1. The sols usually contain a small amount of coarser, probably flocculated material which sediments very rapidly under the experimental conditions. Since only its mean size can be estimated, this portion is indicated as a rectangle of the proper relative area at the right of the primary distribution curve. A shift in mean radius from 3.8 to 4.4 millimicrons occurred during the first 23.5 hours as a result of the dialysis. The change is so small, however, that it is safe to conclude that the particle size of the hydrous ferric oxide is not greatly affected by the elimination of the acid and salts. The slight

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[1] Knop: J. Am. Chem. Soc., **46**, 263 (1924).

change probably results from the appearance of new ferric oxide formed by the hydrolysis of ferric chloride in the intermicellar liquid, for, owing to the greater mobility of hydrogen ion, the acidity of the solution was reduced sufficiently to permit additional formation of ferric oxide before the ferric chloride present was dialyzed out.

After 24 hours' further dialysis the mean radius appeared to decrease slightly instead of increasing further. This shift, however, may not represent a real difference in particle size but merely a hindered sedimentation caused by what may be called a Donnan effect.[1] A re-examination of the purified sol a month after the dialysis showed a noticeable increase in turbidity, and the mean radius of the particles was found to be nearly 6 millimicrons. Therefore, the dialysis had brought down the electrolyte content to a point of reduced stability.

The absence of marked changes in particle size during dialysis is certainly not a general phenomenon. For the particular sol investigated, the concentration of electrolytes presumably was sufficient to maintain stability, but insufficient to cause aggregation, for, otherwise, reduction of the electrolyte concentration would probably have led to peptization of the aggregates and a shift in the distribution curves to smaller sizes. On the other hand, the concentration of electrolytes was more than sufficient to maintain stability, for removal of them to a point represented by a purity of 44 did not lead immediately to detectable aggregation. The absence of a change in particle size upon reversing the charge with potassium citrate[2] also indicated that the particles are largely primary particles.

Effect of Aging

Aging is a vague term applied to colloidal material, which in this case includes spontaneous changes in particle size, changes in distribution of ions between the intermicellar liquid and the micelle, reversal of hydrolysis or resolution of the particle, and many other factors. Data on two of these factors are given below, namely, the reversal of hydrolysis, and the change in the distribution curve.

Changes in Composition: Table II gives the analytical results obtained for a freshly prepared, undialyzed sol and for a three-months-old, undialyzed sol from the hydrolysis of 0.037 M FeCl$_3$. The colloidal and the ionic iron were separated by precipitating the colloidal fraction with equal volumes of 0.0025 M K$_2$SO$_4$ and throwing out and washing the precipitates in a laboratory centrifuge. It is evident that the colloidal iron content dropped in the three-months interval from 77% to only 37% of the total iron present, with a corresponding increase in the ferric chloride content of the intermicellar liquid. The small amount of chlorine which was found in the precipitate of

[1] Tiselius: Z. physik. Chem., **124**, 457 (1926); Nichols: Sixth Colloid Symposium, 298 (1928).

[2] Nichols, Kraemer, and Bailey, Part I loc. cit. p. 332.

ferric oxide is designated as non-displaceable because the coagulating sulfate ion is able to displace much of the chlorine from the micelle.[1]

The rate of reversal of course depends upon the concentration of the system. In the same period of time, re-solution would undoubtedly occur to a greater extent in more concentrated sols and to a lesser extent in more dilute sols.
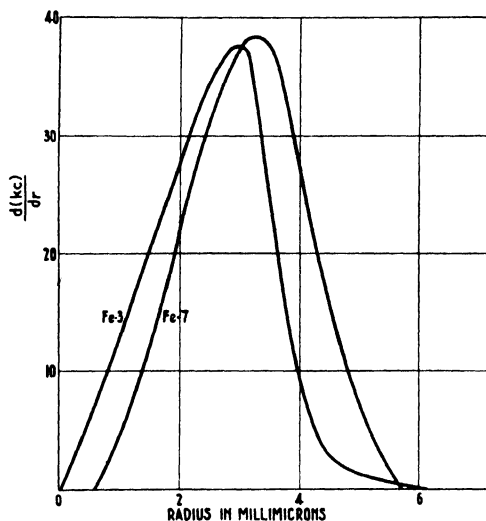
FIG. 2

EFFECT OF AGE ON THE WEIGHT-OPTICAL DISTRIBUTION CURVE OF FERRIC OXIDE FROM 0.005 M FeCl$_3$

Sol	Age (Days)	Weight-Optical Mean Radius	Area
Fe-3	1	2.6 mμ	89%
Fe-7	15	3.1	99

TABLE II

Change in Colloidal Iron Content on Aging of Ferric Oxide Sols

Sol (From 0.037 M FeCl$_3$)	Age (Days)	Total Fe Content g.eq./l.	Total Cl Content g.eq./l.	Colloidal Fe Content g.eq./l.	Non-Displaceable Colloidal Cl Content g.eq./l.
IV	1	0.1163	0.1120	0.0898	0.00090
II	95	0.1161	0.1123	0.0427	0.00104

Changes in Particle Size: Aging seems to affect somewhat differently the distribution curves of ferric oxide sols prepared from different concentrations of ferric chloride. The distribution curve of ferric oxide from rather dilute (0.005 M) ferric chloride (Fig. 2) undergoes only a shift to a slightly larger mean size, but the distribution curve of the ferric oxide from the more concentrated (0.037 M) ferric chloride (Fig. 3) becomes somewhat flatter on aging and shows a considerable increase in the amount of secondary material of about 20 millimicrons in radius.

[1] Cf. Linder and Picton: J. Chem. Soc., **87**, 1908 (1905); Weiser: J. Phys. Chem., **35**, 10 (1931).
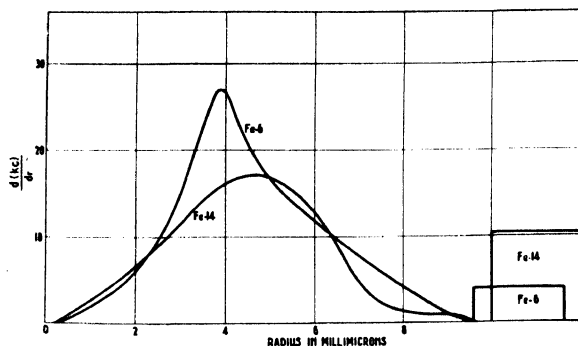
Fig. 3

EFFECT OF AGE ON THE WEIGHT-OPTICAL DISTRIBUTION OF FERRIC OXIDE
FROM 0.037 M FeCl$_3$

Sol	Age (Days)	Primary Mean Rad.	Primary Area	Secondary Mean Rad.	Secondary Area
Fe-6	1	4.4 mμ	90%	ca. 20 mμ	8%
Fe-14	72	4.6	76	ca. 20	21

Effect of Dialysis on an Aged Sol

In view of the difference in composition of fresh and of aged sols, it seems likely that dialysis would have a different action in the two cases; for instance, the aged sol is conceivably more stable than the fresh sol, or it might contain secondary material which would be re-peptized during dialysis. A 2.5-months-old sol (prepared from 0.037 M FeCl$_3$), which contained much ferric chloride formed by the re-solution of some of the ferric oxide was used for this study. Samples were removed after 4, 8 and 20 hours of dialysis of a 300 cc. portion of the sol at 25°C. After eight hours the dialysate gave only a faint test for iron with thiocyanate solution, but a positive test for chloride with silver nitrate. At the end of twenty hours no test was obtained for either constituent in the dialysate.

Changes in Composition: Table III gives the compositions of the series of samples obtained, after correction for the osmotic dilution occurring during

TABLE III

Effect of Dialysis on 2.5 Months Old Ferric Oxide from 0.037 M FeCl$_3$

Sample	Time of Dialysis (Hours)	Total Fe g.eq./l.	Total Cl g.eq./l.	Purity	Colloidal Fe g.eq./l.	Ionic Fe or Cl as FeCl$_3$ g.eq./l.	Hydrochloric Acid Cl g.eq./l.
Fe-30 (original)	0	0.1161	0.1123	1.0	0.0426*	0.0735*	0.0372
Fe-26	4	0.0748	0.0271	2.8	0.0650	0.0098	0.0157
Fe-28	8	0.0735	0.0104	7.1	0.0698	0.0037	0.0051
Fe-29	20	0.0715	0.0016	43.3	0.0715	—	—

*Separation of colloidal and ionic iron by precipitation with potassium sulfate solution gave 0.0427 g. eq./l. of colloidal iron and 0.0734 g. eq./l. ionic iron.

the dialysis. The table shows that the sol reached the same purity as the fresh sol. It is also evident that the colloidal-iron content after twenty hours of dialysis increased nearly 70% over that of the undialyzed sol. This indicates that the removal of hydrochloric acid at the start of the dialysis permitted a re-hydrolysis of much of the ferric chloride or basic ferric chloride present. The total loss in iron during the dialysis amounted to about 39%.

The colloidal-iron content (corrected for osmotic dilution) was calculated on three assumptions: First, that the chlorine and iron present at the end of the dialysis (sol Fe-29) were all contained in the micelle; second, that the light absorption was due to the colloidal-iron content; and third, that Beers' law holds. This procedure is justified by the agreement between the colloidal iron of Fe-30 estimated colorimetrically and the value obtained by precipitation of the colloidal fraction with potassium sulfate solution. Ionic iron (column 7) was considered as the difference between total iron and colloidal iron.

In estimating the distribution of chlorine, the ionic iron was assumed to be present as ferric chloride. Accordingly, column 7 refers to both the iron and the chlorine of the ferric chloride. The remaining chlorine was present in part as chlorine bound in the colloidal micelles, which was supposed to be equal to chlorine still present at the end of dialysis (Fe-29, column 4), and in part as hydrochloric acid. The values of column 8 were therefore obtained by subtracting the bound chlorine and the chlorine as ferric chloride from the total chlorine content.

The table shows that the re-hydrolysis of the ferric chloride, which took place as a result of the more rapid removal of hydrogen ion than of ferric ion during the dialysis, proceeded rapidly in the first four hours and practically reached completion at the end of eight hours. As long as the re-hydrolysis proceeds some of the chlorine will be present as hydrochloric acid formed during this process; accordingly, it was not possible to estimate the ionic iron in the earlier stages simply from the chlorine content found.

Changes in Particle Size: The weight-optical distribution curves for the series (Fig. 4) also show that most of the change occurred in the first four hours. The distribution curve for the eight-hour sample (Fe-28) was practically identical with that for the four-hour dialysis; therefore, the former was left out of the figure to avoid confusion of lines. Its mean radius was 4.5 millimicrons as compared with 4.55 millimicrons for the sample taken after four hours of dialysis. Reduction in the hydrogen-ion concentration in the early stages of the dialysis seems to produce both a re-hydrolysis of ferric chloride present and a re-peptization of some of the flocculated material, represented by the rectangles at the right of the distribution curves.

Comparison of the distribution curves for the dialyzed sols of an aged ferric oxide (Fig. 4) with those for the dialysis of a fresh ferric oxide sol (Fig. 1), and with the curves in Fig. 3, giving the effect of aging on the distribution curve, shows that, even when the electrolytes have been largely eliminated, the flattened form of distribution curve is retained for the aged sol and the steeper type is retained for the freshly prepared sol. Aging there-

fore seems to produce some permanent change in the shape of the distribution curve for the more concentrated sol.

It is not possible to decide from the distribution curves whether the material hydrolyzed during the dialysis was simply deposited on the particles already present, thus shifting the mean radius to a slightly larger size, or whether new primary particles of larger mean size were formed from the hydrolysis of the ferric chloride present in the sol. The distribution curves for both the freshly hydrolyzed and for the aged ferric oxide showed a slight
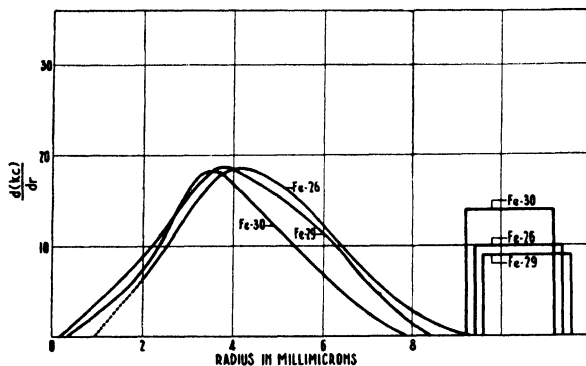
FIG. 4

EFFECT OF DIALYSIS ON THE WEIGHT-OPTICAL DISTRIBUTION CURVE OF TWO-AND-ONE-HALF MONTHS OLD FERRIC OXIDE FROM 0.037 M FeCl$_3$

Sol	Time of Dialysis (Hours)	Primary Mean Rad.	Primary Area	Secondary Mean Rad.	Secondary Area
Fe-30	0	3.80 mμ	64%	ca. 20 mμ	28%
Fe-26	4	4.55	80	ca. 20	20
Fe-28*	8	4.50	82	ca. 20	18
Fe-29	20	4.20	82	ca. 20	18

*Distribution curve for Fe-28 omitted to avoid confusion of lines.

shift to a smaller mean size when the sols were sufficiently free from electrolytes. This shift may well be caused by the entrance of a slight Donnan potential.[1]

Effect of Age on Light-Absorption Relations

During the aging of the more concentrated sol the light absorption in the visible decreased to about one-half its original value on account of the conversion of some of the highly absorbing hydrous ferric oxide to ferric chloride, which by comparison has a negligible absorption in the visible. This conversion is more directly revealed by comparison of the ultraviolet absorption of the sols and of the intermicellar liquid remaining after centrifuging out the colloid particles. For a fresh sol the intermicellar liquid contributed 12% of the total absorption at 366 millimicrons, whereas after 2.5 months the intermicellar liquid accounted for 37%. The absorption of the intermicellar liquid is undoubtedly largely due to the ferric chloride.

[1] Tiselius: loc. cit.

Dialysis of a freshly prepared sol brought about a large increase in light absorption without much increase in the colloidal-iron content. Evidently the composition of the particles changed during dialysis even though the rate of sedimentation did not. The change possibly involved the removal of chlorine from the colloidal particles (which would tend to decrease their density) and a simultaneous dehydration and condensation of the particles (which would tend to increase their density). The absorption relations for an aged sol were much simpler, however. The composition of the micelle had probably approached an equilibrium with the intermicellar liquid, which was not much changed by the removal of electrolytes during dialysis. Under these conditions, as was shown in Table III, it was possible to calculate the colloidal-iron content from colorimeter measurements. It is intended to investigate the light-absorption relations further with the view of obtaining quantitative data on the changes undergone by the sols during aging.

Effect of Age of Stock Solution

During the course of this investigation a single stock solution of ferric chloride was used. The stock solution, however, was not entirely stable, as is demonstrated by particle-size analyses of sols made at various ages of the stock (Table IV). It is evident that there is a gradual decrease in the weight-optical mean radius from 4.4 millimicrons for a sol prepared from the two-weeks-old stock solution to 3.85 millimicrons for the sol prepared from the

TABLE IV

Effect of Age of 1.87 M FeCl$_3$ Stock Solution on the Ferric Oxide Sol Produced

Fe$_2$O$_3$ Sol (From 0.037 M FeCl$_3$)	Age of Stock Solution	Weight-Optical Mean Radius of One-Day-Old Sol
Fe-6	2 weeks	4.40 mμ
Fe-19	3 months	4.05
Fe-31	8 months	3.85

eight-months-old stock solution. Probably the explanation for this gradual decrease in mean radius lies in the production of more and more nuclei in the stock solution as it grows older. Thus, when the diluted ferric chloride was hydrolyzed the particles would have more centers on which to form, and therefore the mean size would be smaller since the same concentration of ferric chloride was used in each hydrolysis. The nuclei might be semi-colloidal basic ferric chlorides resulting from a slight hydrolysis.

It is a pleasure to acknowledge the assistance given by Mr. E. S. Wilkins of our Analytical Department in making the chemical analyses.

Conclusions

Colloidal solutions formed by boiling dilute ferric chloride solutions are unstable, the hydrolytic reaction being reversed upon standing at room temperatures by conversion of the colloidal hydrous ferric oxide to ferric

chloride.   For instance, in a fresh sol containing 0.116 gram equivalents iron per liter, about 80% of the iron is in the form of colloidal ferric oxide, whereas after 2.5 months the colloidal fraction falls to about 40%.

During aging, the particle-size distribution as determined with the ultra-centrifuge shifts slightly toward larger sizes, the change becoming greater and the formation of secondary aggregates being more pronounced in the concentrated sols.   Apparently two opposing processes occur during aging: Re-solution of colloidal particles, especially the smaller ones, and aggregation of the larger particles.   The initial particles are probably primary particles 3 to 4 millimicrons in radius for total iron concentrations below $0.037M$.

Dialysis of both fresh and aged sols leads to hydrolysis of some of the ferric chloride in the intermicellar liquid and to formation of additional colloidal ferric oxide; the particle-size distribution is, however, not appreciably changed at the end of the dialysis.   However, the colloidal matter in the purified sol grows more rapidly than before.

Changes in the sols during aging or dialysis are also revealed by changes in light absorption, owing to the much greater absorption by colloidal iron than by ionic iron.   Concentrated ferric chloride solutions change slowly at room temperature, presumably by hydrolysis and formation of semi-colloidal particles, for the particle size of sols formed upon diluting and boiling decreases somewhat with the age of the concentrated stock solution.

Wilmington, Delaware,
September 15, 1931.

THE ANALYSIS OF ALUMINUM SULPHATE*

BY WILDER D. BANCROFT, HERBERT L. DAVIS AND ESTHER C. FARNHAM

In the course of some work on the preparation and properties of alumina lakes, it became necessary to analyze the aluminum sulphate used. This analysis met with some apparent difficulties which finally found their explanation that the kilogram of salt used from the original bottle of the manufacturer was not homogeneous but contained two lots of salt of distinctly different water content. Early analysis of material from the top of the bottle revealed a neutral salt which averaged 44.75% water while the bulk of the sample was 47% water. These correspond roughly to 15.5 and 17 molecules of water as compared with the theoretical 48.7% water in the octadecahydrate. Such a situation in the case of a highly hydrated salt and one capable of losing a portion of its water of hydration under even moderate conditions, indicates that some of the textbooks might well include some suggestion as to sampling such a specimen analogous to that employed in bulk materials. As this particular sample was analyzed the alumina content of an early sample from the top was distinctly higher than would correspond to the sulphur trioxide found by a subsequent analysis of another sample from the bulk of the material. Before the true explanation of the phenomenon was found, various hypotheses were tested to see if they explained the apparent low weight of barium sulphate precipitated from a solution of aluminum sulphate. There are in the literature actual statements and ample theoretical considerations to lead one to expect low results in this determination and the present paper is designed to demonstrate that when certain slight changes are made in the procedure, aluminum salts do not interfere with the sulphate determination to anything like the degree shown by iron or chromium salts which are in so many other ways comparable substances.

Some of the difficulties encountered in the precipitation of sulphates with barium chloride have been discussed by Treadwell-Hall.[1]

"Here the relations are far more complicated than in the precipitation of pure sulphuric acid, partly because the barium sulphate is more soluble in salt solutions than in water containing a little acid, and partly because of the tendency of barium sulphate to occlude not only barium chloride but many other salts as well. Solutions of chromium sulphate are either violet or green. From the boiling hot green solution only one third of the sulphuric acid is precipitated, the remainder probably being present in the form of a complex chromium sulphate cation; on cooling, the green solution gradually

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[1] Treadwell-Hall: "Analytical Chemistry, Quantitative," 402 (1928).

becomes violet and, after some time, all of the sulphuric acid is precipitated. The precipitation of barium sulphate in the presence of ferric iron has been much studied. In the boiling hot solution all of the sulphuric acid is not precipitated and considerable iron is thrown down with the barium sulphate and furthermore the precipitate then loses SO_3 on ignition. Since ferric oxide weighs less than an equivalent weight of barium sulphate, sometimes the results are as much as ten percent too low. On the other hand, Küster and Thiel[1] were able to get satisfactory results: (1) by precipitating the sulphuric acid from such a solution in the cold; (2) by adding the ferric chloride and sulphuric acid solution slowly to the hot solution of barium chloride; or (3) by precipitating the iron by an excess of ammonia, heating, and adding barium chloride to the solution without filtering off the ferric hydroxide, and finally dissolving the latter in dilute hydrochloric acid.

"Most chemists, however, deem it advisable to remove tervalent metals before attempting to determine the sulphuric acid. This is accomplished in the case of ferric iron by adding a liberal excess of ammonia to the dilute, slightly acid, solution which is at a temperature of about 70°. If from 5-7 ml. of concentrated ammonia is added in excess to the amount required for neutralization,[2] the precipitate is not likely to contain any basic sulphate. If, on the other hand, the solution is barely neutralized with ammonia, the precipitate will invariably contain some sulphate."

A rather detailed discussion of the plus and minus errors in the precipitation of $BaSO_4$ is given by Hillebrand and Lundell[3] who infer that aluminum has some effect when they outline a method "designed primarily for the determination of large amounts of the sulphate ion in solutions containing considerable iron, as with pyrite, and moderate amounts of other substances such as aluminum, zinc or calcium." This method consists in adding very dilute barium chloride slowly and in the cold to a very dilute (1600 cc) solution of the sulphate, letting stand over night and filtering, and igniting in the usual way.

The obtaining of high results in this analysis is somewhat unusual but was reported by Creighton[4] who precipitated constant amounts of ammonium sulphate solutions in the presence of increasing amounts of aluminum chloride and obtained a nice adsorption curve when he plotted excess weight against amount of aluminum chloride added. His error was never as great as one percent of the total weight and was attributed by him to the formation of a solid solution of alumina in the barium sulphate.

Far more usual are the reports of low weights of barium sulphate from such solutions. It appears that, in addition to the errors already mentioned, there may also enter an adsorption of sulphate ion by the colloidal alumina always present in such solutions of aluminum sulphate in the absence of high acid concentrations to repress the hydrolysis. On the addition of barium

[1] Küster and Thiel: Z. anorg. Chem., **22**, 424 (1900).
[2] Pattinson: J. Soc. Chem. Ind., **24**, 7 (1905).
[3] Hillebrand and Lundell: "Applied Inorganic Analysis," 572 (1929).
[4] Creighton: Z. anorg. Chem., **63**, 53 (1910).

some barium sulphate may be formed on the colloidal alumina and thus be protected from precipitation. This seems to be the explanation of the work of Fraps[1] who attempted to explain the fact that "considerably more barium sulphate was obtained when the iron and aluminum had been previously precipitated from the soil solutions." He observed the amounts of equivalent barium chloride and sulphuric acid solutions which needed to be added to solutions of $AlCl_3$, $FeCl_3$, or $MgCl_2$ in order to give a visible precipitate in 48 hours. This gave values of 175, 170 and 50 mg. of barium sulphate respectively dissolved in a liter containing 100 g. of these salts. These values are probably not to be taken too seriously for these are concentrated solutions of salts; but the relative values are of some interest.

Such must also be at least a part of the explanation of the interesting work of Küster and Thiel referred to above. The experiments showed that only if certain changes can be made in the procedure is it possible to precipitate all the sulphuric acid from solutions containing iron salts. These changes involved the previous removal of the ferric iron either by precipitation with ammonia or by conversion into a complex with ammonium oxalate or the selection of conditions in which the hypothetical $Ba(Fe(SO_4)_2)_2$ could not form. These conditions were by precipitation in the cold or by pouring the ferric chloride and sulphuric acid into the boiling barium chloride instead of the reverse process. It is quite evident that there are two sources of error in this determination. In the whole series of experiments none gave the correct weight for $BaSO_4$ if the ferric chloride had been heated with the sulphuric acid, for then the hydrous colloidal ferric oxide adsorbed the sulphate ion strongly and carried some of it into the precipitate as a basic ferric sulphate complex and carried a part of it through the filter paper by its protective action. Even if all the sulphate ion were in the precipitate the observed weight will be too low if a part of the sulphate is present in the iron complex. An indication that all the sulphate does not enter the precipitate is shown by an observation. "A very remarkable difference was noted in the precipitation of the iron-free and the iron-containing sulphuric acid: in the former liquid the first drop of barium chloride produced a definite precipitate, in the latter however twelve or thirteen drops were required." Equally good evidence of the co-precipitation of iron is found in the observation that in each case those precipitates which were low in weight were also red while the correct runs produced white precipitates. That the hydrolysis is important is shown by the fact that the deficiency of weight of the $BaSO_4$ was 0.04% at 17°, 3.45% at 50°, and 6.10% at 100°. Better results were obtained in using small total volumes and in adding rather large excess of hydrochloric acid. Low temperature, small dilutions and high acidity repress the hydrolysis of ferric salts and therefore the errors thus introduced.

The adsorption of sulphate ion on alumina has been reported and measured by many workers. One of the most exaggerated of these cases is that of Sacker[2] who confirmed previous work by Buchner to the effect that when

[1] Fraps: Am. Chem. J., 27, 288 (1902).
[2] Sacker: Chem. Ztg., 35, 1447 (1911).

concentrated solutions of aluminum sulphate were mixed with concentrated solutions of barium acetate the clear viscous liquid produced deposited barium sulphate only after long standing, on scratching the side of the vessel, warming slightly, or dilution. A major factor here is the well-known tendency of barium sulphate to form colloidal systems under such conditions even in the absence of aluminum salts. Nevertheless Sacker reports that aluminum sulphate is more effective than magnesium or sodium sulphate in retarding the precipitation of barium sulphate. This points to a protective action from the alumina in the solution of aluminum acetate.

Consideration of this direct evidence concerning aluminum salts and of the more voluminous evidence concerning the analogous ferric salts made it quite reasonable to expect that a similar explanation would apply to our results for the apparent low sulphate determinations. It is found, however, that the determination of sulphate from solutions of aluminum sulphate is attended by no such difficulties and that the relatively slight error may be minimized by the addition of hydrochloric acid to the dry salt or to a concentrated rather than a dilute solution of the salt. The purpose of this is to repress the hydrolysis more effectively and to redissolve any basic sulphate which might be present. Such a basic sulphate, unless it were very strongly basic, would weigh less than an equivalent weight of barium sulphate and would lose sulphur trioxide on ignition. Unless dissolved, this basic sulphate, which is the usual cause of the turbidity in commercial aluminum sulphate solutions, would be carried down mechanically and adsorbed on the barium sulphate.

That the presence of aluminum chloride has a very slight effect on the weight of barium sulphate obtained is shown by a simple series of experiments. In these experiments 50 cc samples of a dilute sulphuric acid were precipitated in 200 cc by the addition of about 9% excess barium chloride in dilute solution. A blank run gave 0.7996 g $BaSO_4$. When an equivalent amount of aluminum chloride solution was added to the sulphuric acid and then barium chloride added to the hot solution, 0.7961 g $BaSO_4$ resulted. But the basic sulphates which might interfere would have little chance to form under such conditions. Therefore a mixture of 50 cc of the sulphuric acid and 6.8 cc of N $AlCl_3$ solution was evaporated and then heated overnight in an oven at 110°, giving 0.7946 g $BaSO_4$, while a similar mixture heated for 45 hours at 110° gave 0.7930 g $BaSO_4$. But such systems are all strongly acid as they evaporate and low acidity would greatly favor the formation of basic sulphates. Therefore the sulphuric acid was neutralized with sodium hydroxide, aluminum chloride added as before and the solutions evaporated and solid finally dried for 20 hours at 110°. The weights of barium sulphate obtained averaged 0.7963 g. It is therefore clear that in the precipitation of barium sulphate by adding barium chloride to the aluminum sulphate no error greater than 0.7% can be demonstrated. By heating to a high temperature it is of course possible to drive off part or all of the sulphur trioxide but such treatments are not given to commercial salts in drying.

In actuality the first method of analysis tried on the sample at hand was a thermal treatment, it being thought possible to drive off the water of hydration at a moderate temperature and then by a blast lamp to drive off the sulphur trioxide, thus giving all the necessary data. This procedure appears quite practicable and will be reported. Crystalline aluminum sulphate has been described as containing, under various conditions, 27, 18, 16, 12, 10, 9, 6, 3, and $2H_2O$ and the weight of evidence indicates that the hydrate which crystallizes under ordinary conditions is the familiar $Al_2(SO_4)_3 \cdot 18H_2O$. A clue to a possible method of analysis is given by Friend.[1] "Aluminum sulphate, $Al_2(SO_4)_3$, is prepared in the anhydrous state by heating the crystalline hydrated salt. The latter melts in its water of crystallization, swells up, and eventually leaves a white porous residue of a hydrous sulphate. At a red heat it decomposes, leaving a residue of alumina; decomposition becomes appreciable at 770°." Essentially the same information is given by Mellor[2] in greater detail. The literature indicates that at 770° the vapor pressure of sulphur trioxide and its decomposition products from the aluminum sulphate exerts a pressure of one atmosphere, and further that alumina is not affected by temperatures below 1500° at least. It is not clear how hot the hydrate may be heated in order to drive off all the water and to avoid expelling any sulphur trioxide. Dudley[3] drove off all but five percent of the water by heating a sample at 350°. He was not interested in obtaining anhydrous salt and expelled the rest of the water along with the sulphur trioxide at 735°. It appeared probable that one could dehydrate the salt at about 300° without appreciable decomposition of the anhydrous salt. Further support for this scheme of analysis is found in the directions of Treadwell-Hall.[4] "If the solution contains only aluminum in the form of its chloride, nitrate, or sulphate, it can be determined by evaporating the solution in a platinum crucible on the water-bath with the addition of a little sulphuric acid, the excess of the latter being finally removed by cautious heating over the free flame in an inclined crucible. The residue of aluminum sulphate can be changed to the oxide by strong ignition over the blast-lamp."

In the first use of this method, samples of the hydrate from the top of the stock bottle were weighed in platinum dishes, one cc of N H_2SO_4 was added to each, and they were heated very slowly, the final heating being done over a free flame with a thermometer suspended just above the surface of the powder, the temperature being permitted to go no higher than 250° as read thus. About a half hour's heating sufficed to give constant weight, the samples being stirred and the aggregates broken by means of a glass rod. Vigorous blast-lamp treatment then converted the salt into alumina. The average of these determinations is shown in Table I.

[1] Friend: "A Text-Book of Inorganic Chemistry," 4, 80 (1917).

[2] Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 5, 334 (1924).

[3] Dudley: Met. Chem. Eng., 13, 303 (1913).

[4] Treadwell-Hall: "Analytical Chemistry," 2, 94 (1928).

	Al_2O_3	SO_2	H_2O
Sample from top of bottle	16.51%	38.74%	44.75%
$Al_2(SO_4)_3 \cdot 18\ H_2O$	15.32	36.03	48.65

Samples of the same salt showed by precipitation 16.55% Al_2O_3, in satisfactory agreement with the above. Further confidence in the thermal analysis was given by the fact that the residue of alumina was equivalent to the sulphur trioxide calculated by difference above. Also tests showed the salt to contain no appreciable free acid or base. Nevertheless repeated sulphate precipitations from samples taken somewhat later and farther down the stock bottle gave consistently 37.18% SO_3 instead of the 38.74% shown by thermal analysis. It was in the unraveling of this apparent discrepancy that this work was done. The real answer was found in repeating the thermal analysis on a second sample of salt taken farther down the bottle after some had been used. In the meantime had appeared the report on the thermal decomposition of alunite, $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$, in which the authors[1] say: "The temperatures suggested can be classified into three groups: 500°-750°C., 750°-1000°C., and 1000°-1600°C. Although there are a number of contradictory claims in the patent literature, it would appear that in the first range, acid-soluble sulphates are probably formed; in the second K_2SO_4 and Al_2O_3; and in the third, either alumina and K_2SO_4 vapor, or potassium aluminate. . . . Samples of alunite heated from 18 to 48 hours at 250°-500°C. gave only the sharp x-ray reflections characteristic of the rhombohedral lattice of the untreated alunite. A sample heated 20 hours at 600°C. gave a diffuse pattern indicating very small or imperfectly formed crystals of a new phase (X) and a trace of residual alunite. A specimen subjected to a thirteen-hour treatment at 700°C. produced only the sharp diffraction lines of phase (X). . . . X-ray diffraction methods were advantageously applied in the identification of phases (X) and (Y). The composition of alunite would indicate that the phase X might be aluminum sulphate, potassium sulphate, or a double sulphate of aluminum and potassium. The pattern of phase X was entirely different from that of K_2SO_4 or $Al_2(SO_4)_3$ which had been heated at 700°C. for 16 hours. Consequently a series of samples was made containing various molecular ratios of anhydrous aluminum and potassium sulphates and treated for 32 hours at 700°C. The x-ray photogram of the sample synthesized from equimolecular quantities was identical with that of phase X."

There appears to be no good way of judging the sensitivity of such a procedure for the detection of small quantities of a new phase but from the above it appeared that the aluminum sulphate might be heated to at least 400° without driving off SO_3. Therefore a new run was made in which the first heating was carried out in a muffle furnace. During the first 2.5 hours the temperature rose slowly to 325° and the samples lost 45% of their weight. During the next 16 hours at 400° C. they lost only one more percent. These dehydrated samples were then analyzed for sulphate and afterwards for alumina by precipitation. The dehydrated salts went into solution readily,

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[1] Fink, Van Horn, and Pazour: Ind. Eng. Chem., **23**, 1248 (1931).

producing a slight turbidity which was nearly completely cleared by the acid addition to the salt in a small volume of water and then heating to boiling. The alumina determination by precipitation from the dehydrated salt agreed exactly with alumina as found by blast lamp treatment on a different sample of this same bulk of material in the bottle. The analysis of the main bulk of the material is shown as Al_2O_3, 15.76%; SO_3, 37.21%; H_2O, 46.0%. Again the SO_3 is equivalent to the alumina and is about that found by a large number of analyses using the suggestions mentioned above for the iron sulphate determinations. There is in this last thermal decomposition a missing one percent which is undoubtedly residual water still left in the salt. This shows that the composition of the main bulk of material is an average of $Al_2(SO_4)_3 \cdot 17\ H_2O$.

Various methods give concordant results for this analysis. One set of samples dehydrated at $400°C$. lost 46% of their weight as the water. This same material was then dissolved (with only a slight turbidity, largely cleared by the ordinary addition of hydrochloric acid) when the SO_3 content found was 37.10% and the alumina content was 15.76%. Thus heating in the blast lamp gave exactly the same alumina content as precipitation after removal of the sulphate. The dehydrated aluminum sulphate showed slightly less SO_3 than the salt analyzed without dehydration. It appears quite possible that a shorter heating, possibly up to $500°C$., would drive off the water with little or no loss in SO_3. Of course the temperature of about $750°$ has no unique significance in the temperature-pressure curve of sulphur trioxide from aluminum sulphate, and decomposition begins far below that. It merely becomes a question of how high the temperature can be raised to give most rapid dehydration and least decomposition.

Finally it may be added that before the simple solution of our difficulty was found we tried several of the special methods suggested above for the accurate analysis of sulphate in iron solutions. The methods using ammonia were least useful for the large excess recommended for iron peptized large amounts of the alumina instead of aiding their removal as in the case of iron. Precipitation of barium sulphate in alkaline solution or even from cold solutions is very likely to yield precipitates too fine to be caught properly on filter papers. In general, however, none of these methods applied to our aluminum sulphate gave results which differed by more than one tenth of one percent for the sulphur trioxide content of the salt from the value obtained by the dropwise addition of barium chloride to a hot solution of aluminum sulphate.

Conclusions

1. In the precipitation of barium sulphate from solutions of ferric sulphate large errors arise from the adsorption of sulphate ion on the hydrous ferric oxide resulting from the hydrolysis. Inclusion of such basic sulphate complexes in the barium sulphate precipitate as well as retention of a thus protected barium sulphate in colloidal solution are responsible for the low results obtained.

2.   The lower degree of hydrolysis of aluminum salts minimizes both these errors until they are practically negligible. The consequence is that, although in so many other respects aluminum salts are analogous to ferric salts, they present no particular problem in this determination. The hydrolysis they do show may be better repressed and any basic salt dissolved, if the addition of hydrochloric acid be made before rather than after the dilution which usually precedes precipitation of barium sulphate.

3.   A series of comparable experiments shows that the presence of an equivalent amount of aluminum chloride in the precipitation of barium sulphate involves not more than 0.7% error as contrasted with as much as ten percent error in iron solutions.

4.   The contents of an original stock bottle of aluminum sulphate as received has been shown to contain two distinctly different portions as shown by their water content. This may have arisen in the unequal drying (and partial dehydration) of portions of the batch as made or from temperature gradients in storage over portions of the bottom. Whatever its cause, a method of mixing and systematic sampling previous to such analyses and use is shown to be advisable.

5.   It is shown that the water from hydrated aluminum sulphate may be removed practically completely by heating to $400°-500°C$. without significant loss of sulphur trioxide. The anhydrous salt can then be decomposed to alumina over the blast lamp. Such determinations of water, sulphur trioxide, and alumina by thermal decomposition agree very well with the values obtained by precipitation methods.

Cornell University.

THE EFFECT OF THE DILUTING ACTION OF CANE SUGAR UPON THE VISCOSITY OF THE COLLOIDAL SUSPENSION SKIM MILK*

BY ALAN LEIGHTON AND ABRAHAM LEVITON

The apparent viscosity of a given colloidal suspension is the resultant of two major factors, i.e., the viscosity of the liquid phase of the suspension and the ratio of the volume of the dispersed phase to the total volume of the suspension. The addition of a highly soluble non-electrolyte in considerable quantity to such a suspension will, of course, increase the viscosity of the liquid phase of the suspension, but it apparently has never been pointed out that the resulting increase in volume of the liquid phase may so dilute the suspended phase that in highly concentrated suspensions the actual viscosity of the whole system is lowered by the simple presence of the non-electrolyte.

This appeared to be the explanation of the fact that the viscosity of a certain ice cream mix of high fat concentration was, upon homogenization, greater before than after cane sugar was added. Sucrose is referred to in the literature as a peptizing agent.[1] But cane sugar, upon going into solution in water, increases the volume of the water by an amount practically equal to its own solid volume.[2,3] A careful study of the conditions existing in the ice cream mix indicated that the diluting effect of the sugar was the major cause of the viscosity lowering. Any specific peptizing action of the sugar would be equivalent to intensifying this diluting action.

If cane sugar could be used to dilute a colloidal suspension, it seemed that the principle might be applied in a novel manner to the separation of milk sugar from highly concentrated skim milk. This separation would make possible the manufacture of ice cream containing a comparatively high percentage of milk-solids-not-fat which yet would not tend to become sandy through the crystallization of the milk sugar. Attempts to separate any considerable amount of lactose from skim milk have not been successful heretofore because of the fact that skim milk concentrated to a degree which will permit of the separation of a high percentage of the lactose is so viscous that the lactose crystals cannot be mechanically separated from the mass; also the viscosity of a highly concentrated skim milk tends to increase rapidly with time. Cane sugar, when added to skim milk, might, upon the concentration of the milk, so dilute the concentrated product, lower its viscosity, and retard thickening that even when a concentration was attained sufficient to crystallize a considerable portion of the milk sugar, a viscosity would result sufficiently low to permit of its mechanical separation from the milk. The addition of cane sugar would also tend to decrease slightly the solubility of

the lactose in the skim milk. From a commercial viewpoint the use of cane sugar would not cause additional expense since cane sugar is a normal constituent of ice cream. To illustrate the extent to which cane sugar adds to the volume of a suspension it may be mentioned that if six grams of cane sugar are added to 100 grams of skim milk and the resulting suspension condensed to have a concentration of 130 parts milk-solids-not-fat to 100 parts of water, the volume of the liquid phase of such a milk would be approximately 1 1/3 times greater than if the cane sugar had not been added.

In view of the possible application of the principle to the separation of lactose, the detailed study of the effect of cane sugar upon the viscosity of a colloidal suspension was made upon the more simple concentrated skim milk rather than upon the more complex ice cream mixes. This paper is, then, an account of experiments undertaken to determine the effect of cane sugar upon the viscosity of concentrated skim milk, consideration being given to the solubility relationships of milk sugar and the practicability of separating it from the condensed product.

To determine the effect of cane sugar upon the viscosities of sweetened condensed milks, concentrated milks of different sugar concentration were prepared as follows: Four-kilogram portions of skim milk were weighed out. If sugar was to be added, it was weighed into the milk. The milks were fore-warmed for fifteen minutes and then were drawn into twelve-liter round-bottomed flasks and concentrated to the desired degree under a vacuum by the distillation of the contained water. Boiling water supplied the necessary heat. The degree of vacuum was such that boiling took place at temperatures between 35°C. and 45°C. A brief series of experiments indicated that the lowest viscosities in the final concentrates were obtained when fore-warming was carried out at normal pasteurizing temperature, i.e., 63°C. The use of higher temperatures gave solutions of higher viscosities. This is in accord with observations of other experimenters.[4,5] The milks were condensed to have an approximate concentration of 130 parts milk solids to 100 parts of water. (The cane sugar is neglected in this expression of concentration). The change of the viscosity with varying milk solids concentration was then determined either directly, or by diluting back weighed portions of the concentrated milk with weighed amounts of water and measuring the apparent viscosities of all concentrations by means of a capillary viscometer. The amounts of sugar that were added to 4000 g. portions of skim milk were as follows: None, 100 g., 160 g., 180 g., 200 g., 240 g., 320 g., 360 g., 420 g., and 500 g. The addition of 500 g. of sugar to four kilograms of skim milk represents a concentration on the milk-solids-not-fat basis that would be present in a normal ice cream and was for that reason the greatest amount of sugar that it seemed advisable to use. The comparative viscosities of the milks of different sugar content at high concentrations are given below, Table I. The figures represent the average of from two to four check concentrations in every case.

TABLE I

Variation of Milk Viscosity with Concentration and Cane Sugar Content

Milk solids conc'n in parts per 100 of water	Viscosity in cp		
	120	130	140
No sugar	460	7500	—
100 g. sugar per 4000 g. skim milk	375	940	1700
160 g. sugar per 4000 g. skim milk	240	380	600
180 g. sugar per 4000 g. skim milk	205	330	500
200 g. sugar per 4000 g. skim milk	215	340	530
240 g. sugar per 4000 g. skim milk	375	620	1075
320 g. sugar per 4000 g. skim milk	900	1500	2600
360 g. sugar per 4000 g. skim milk	1000	1600	2700
420 g. sugar per 4000 g. skim milk	1120	2200	3500
500 g. sugar per 4000 g. skim milk	1700	3300	6000

The viscosity data for a milk-solids concentration of 130 parts milk solids to 100 parts of water are plotted in Fig. 1.

Sugar Content Gms per 4000g Skim Milk
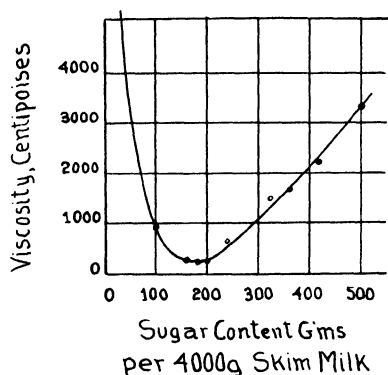
FIG. 1

Comparative Viscosities of Concentrated Skim Milks of Different Sugar Content.

Pts. Milk Solids to 100 Parts of Water

"A" Unsweetened Milk
"B" Sweetened Milk
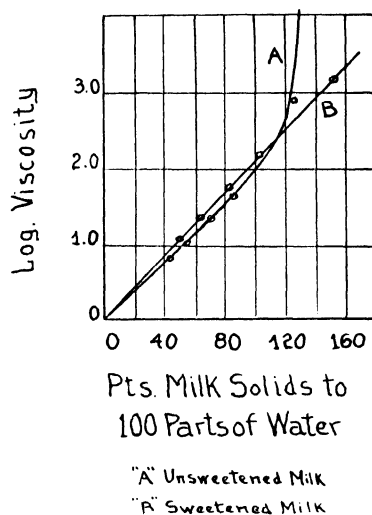
FIG. 2

Comparative Viscosity - Concentration Curves of Sweetened and Unsweetened Concentrated Skim Milk.

It is to be seen that the milk samples containing initially 180 g. of cane sugar to 4000 g. of skim milk exhibit the lowest viscosity, and that the viscosity of the milks containing from 180–300 g. of cane sugar is sufficiently low, even at the high concentrations of the experiment, to permit of filtration or centrifuging of crystallized lactose. Of further interest is the fact that the highly concentrated unsweetened milks were found to thicken very rapidly upon standing at room temperature or below, while the sweetened milks thickened but slowly or not at all.

To aid in discussing more completely the diluting effect of cane sugar, there are plotted in Fig. 2 the complete concentration-viscosity curves for an unsweetened evaporated milk and a milk containing 180 grams of cane sugar to the original 4000 grams of skim milk. The data are recorded in Table II.

TABLE II

Comparative Concentration-Viscosity Relationships of an Unsweetened and a Sweetened Skim Milk

Unsweetened Milk		Sweetened Milk 180 parts cane sugar to 4000 parts skim milk	
Conc'n pts. per 100 of water	Viscosity cp	Conc'n pts. per 100 of water	Viscosity cp
46.2	8.7	50.0	13.3
55.3	11.8	60.8	20.0
70.1	23.3	80.6	53.3
87.7	58.8	102.0	140
127.0	769	150.0	1505
131.0	>7000		

The curves are of particular interest in showing that the logarithmic graph of the variation of viscosity values of the sweetened milk with milk-solids concentration is a straight line throughout its length, at least up to a concentration of 150 parts milk solids to 100 parts of water. This is not true of the unsweetened milk except at the lower concentrations where the graph lies below that of the sweetened milk. At concentrations of from 70 to 80 parts milk solids to 100 parts of water, the graph of the unsweetened milk starts to curve slowly upward, crosses the curve of the sweetened milk at an approximate concentration of 106 parts solids to 100 of water and thereafter rises sharply. The viscosity becomes so great that it is practically impossible to prepare an evaporated milk of a concentration higher than 130 parts solids to 100 of water. It is well at this point to call attention again to the rapid thickening of the evaporated milks at the higher concentrations. Some data on this point are contained in Table III.

TABLE III

Comparative Thickening in a 24-hour Period of a Sweetened and Unsweetened Concentrated Skim Milk

Unsweetened			Sweetened		
Conc'n pts. per 100 of water	Viscosity cp		Conc'n pts. per 100 of water	Viscosity cp	
	Initial	24h		Initial	24h
55.3	11.8	13.3	60.8	20.0	21.0
70.1	23.3	27.6*	80.6	53.3	52.0*
87.7	58.8	120 *	102.0	140	128 *
127.0	769	Solid*	150.0	1505	Heavy* but fluid

* Indicates lactose separation.

It seems logical to assume, in explanation of the data, that when unsweetened milk, upon evaporation of the water, reaches a concentration of from 80 to 90 parts milk solids to 100 parts of water, the concentration is such that the individual protein particles of the milk become so closely packed that the viscosity of the mass increases rapidly and incipient coagulation starts. Coagulation is assumed, since experiment has shown that an evaporated milk of very high concentration does not, upon dilution, attain the original viscosity it had at the lower concentration. On the other hand, in the case of the sweetened milk, the diluting effect of the cane sugar is sufficient to prevent close packing of the protein particles, even at very high concentrations (such as 150 parts milk solids to 100 parts water), and the mass as a whole does not become abnormally viscous; that is, the simple straight line relationship between viscosity and concentration still holds. As an illustration, the sweetened milk of 150 parts milk solids to 100 parts of water has a protein ratio to the volume of sugar solution about the same as the protein ratio to the volume of water of the unsweetened milk of 105 parts concentration to 100 parts of water, a concentration at which the thickening phenomenon has just appeared. As a matter of fact, thickening effects become quite marked as the concentration of the sweetened milk becomes greater than 150 parts milk solids to 100 parts of water. The presence of more sugar at this concentration would probably prevent the thickening action.

If, now, we consider the solubility of lactose and the possibility of separating it from sweetened milks, a study of Fig. 1, would indicate that, while the lowest viscosities in a highly concentrated milk are attained when an initial concentration of 180 parts cane sugar to 4000 parts of skim milk are present, this is necessarily not the best concentration of cane sugar to use when concentrated milks are prepared for the express purpose of the separation of the contained lactose. Lactose is molecularly nearly identical with cane sugar. We would expect its diluting action on concentrated milks to be practically the same as that of cane sugar. Upon the crystallization of lactose, its diluting effect would be lost. It seems logical, therefore, that in the preparation of highly concentrated sweetened milks for the purpose of lactose separation, some additional cane sugar should be put in to compensate, in part at least, for the lactose that will separate. In actual experiments, 240 grams of cane sugar to 4000 grams of skim milk has been found a satisfactory proportion. The percentages of lactose theoretically separable from skim milks of varying concentrations are indicated in Table IV.

TABLE IV

The Amounts of Lactose that can theoretically be separated, at 15°C., from Skim Milks of Varying Concentration

Skim Milk Parts solids to 100 of water	Percent of milk sugar separable	Skim Milk Parts solids to 100 of water	Percent of milk sugar separable
70	53.2	130	74.8
100	67.3	160	79.5

Actually in the laboratory and in semi-works scale experiments it has been found possible to separate from 60 to 75 percent of the total lactose present in skim milks of concentrations from 120 to 150 parts milk solids to 100 parts of water. The work has been done by Dr. Byron H. Webb of the manufacturing section of these laboratories and will be reported by him.

Summary

The work described here has shown that the addition of cane sugar in suitable amounts to skim milk before condensing markedly lowers the viscosity of the highly concentrated product.

This phenomenon can be attributed to the diluting action of the cane sugar on the basis that the dissolved sugar markedly increases the volume of the liquid phase of the suspension.

It has been shown that the increase in liquid volume due to cane sugar may serve not only to decrease directly the viscosity of the concentrated milk but also to inhibit viscosity increase on standing.

It has also been shown that the addition of an optimum quantity of cane sugar to skim milk before condensing reduces the viscosity of the concentrated product to the point where lactose crystallization can take place readily and where separation of the milk sugar crystals by mechanical means is feasible.

Bibliography

[1] W. D. Bancroft and J. E. Rutzler, Jr.: J. Phys. Chem., 35, 144 (1931).

[2] R. Olizy: Bull. assoc. chim. sucr. dist., 27, 60 (1909).

[3] G. Fouquet: Bull. assoc. chim. sucr. dist., 27, 545 (1909).

[4] Greenbank, Steinbarger, Deysher and Holm: J. Dairy Sci., 10, No. 4, 339 (1927).

[5] Emily Grewe and George E. Holm: Cereal Chem., 5, No. 6, 462 (1928).

EVIDENCE OF STRUCTURE IN GELATIN GELS

BY AKSEL G. OLSEN[*]

In 1922 Gortner and Hoffman[1] published data which to them appeared to "indicate that gelatin gels have a structure and that this structure is more or less fixed at the time that gelation takes place." These authors visualize "a crystal structure where the crystals melt or soften at the gelation temperature. The micelles would then be formed by the solidification of crystals and later when micelle touched micelle the hardened surface of the crystal would prevent cohesion." Sheppard and Elliott[2] however, preferred to explain these differences as due to case-hardening and bearing no relation to a crystal structure of the gelatin gels. More recently, however, the view that gelatin gels owe their properties to some form of internal structure has become quite widely accepted. Observations which we have made lead us to postulate that the structure of gelatin gels is that of chains of molecules interlacing in a brushheap fashion, and that in setting of a gel two processes occur, (a) solidification in the usual sense of loss of mobility, and (b) the rather slow building up of chains of molecules. The latter process presupposes some degree of motility of the molecules which are rearranged and on this basis we should expect that gelatin gels set quickly would be composed of rather short chains, only slightly interlaced and therefore more quickly dispersed upon melting than a similar gel solidified very slowly with a maximum opportunity for internal orientation and building up of such structure. On this basis a major difference between weak and strong gelatins may lie in their ability to form long chains.

Now, if these postulates are true we should expect a gel caused to set rapidly by immersion in an ice bath to melt more quickly than a duplicate allowed to set slowly by being held at more elevated temperature. Our observations confirm this view. Also we should expect that a series of jellies made up to the same jelly strength by using proportional amounts of gelatin of different strengths would melt in very different times, depending upon the ability of each particular gelatin to form long interlaced chains of molecules. This also was confirmed by our experiments.

In our observations we have made use of two very simple methods for determining melting and setting time. Incidentally it should be pointed out that melting and setting temperatures of gelatin jellies are rather misnomers as our experience indicates that setting temperature is entirely a matter of *rate* of cooling and only by having that rate infinitely slow can a true setting temperature be observed. The same may be said of the melting temperature, and no doubt the differences observed in these two would approach zero as the rates of cooling and heating respectively approached infinity.

Setting Time

The gelatin solution is placed in test tubes (15 mm. internal diameter) and these immersed in a bath at 50°C. for 15–20 minutes. They are then at once placed in a bath of the desired temperature and observed from time to time. When they can be inverted and show a firm meniscus not deformed by this inversion the gel is considered set. It is well to have more than one tube and to permit the one used for the final observation to remain undisturbed until practically set. This allows of a rather sharp determination.

Melting Time

For melting time observation these same tubes are stoppered, inverted and mounted on a rack immersed in a water bath held at the desired temperature. The meniscus may be observed to gradually rise and become deeply rounded as the jelly softens until finally an air bubble passes up through the jelly. The time interval from immersion until this air bubble rises is recorded as melting time.

Both of these methods are of course empirical and only relative. But using standardized conditions and test tubes of uniform bore, gelatins may be evaluated in a definite numerical way.

Effect of Temperature on Setting and Melting Time

The influence of temperature upon the setting and melting times of gelatin solutions is given in Table I. For these observations a commercial acidified gelatin dessert preparation was used. For melting time observations the tubes of jelly are kept at 14–15° C. for about 18 hours, before being placed in the melting bath.

The results listed in Table I indicate that for both setting and melting point observations the temperature should be maintained within very close limits if comparisons are to be between series tested at different times. It was observed that the time interval between setting and melting materially affects the latter, that is, the melting time of jellies set at 14–15°C. was found to increase with the age of the jelly. However, this maturing did not occur in a jelly set at 0°C. unless the temperature was subsequently raised. These findings are illustrated in Table II which give typical results. Similar results have been obtained repeatedly with jellies prepared with other samples of gelatin.

Evidently at 14–15° there is opportunity for a gradual building up of a complex structure which is broken up again with considerable difficulty, while at 0°–1°C. the setting is so rapid and the jelly becomes so firm that the *maturing* effect, or the gradual molecular orientation, evident at the higher temperature is interfered with. There is then at 0°–1° no complex structure formed, hence the jelly while firm has no permanency, but melts almost at once when it is subjected to melting temperatures.

TABLE I

The Setting and Melting Times of Gelatin Jellies at
Different Temperatures

Temperature °C	Jelly A*		Jelly B*	
	Setting time Minutes	Melting time Minutes	Setting time Minutes	Melting time Minutes
2	13		9	
10	35		18	
14	120		65	
16	240		105	
17	400		175	
19	Not firmly set after 24 hours		Firm after 24 hours	
20	Very soupy after 24 hours		Firm after 24 hours	
22		120		260
23		48		72
24		25		34
25		14		17
27		5		7
30		1½		3

*Jellies A and B prepared with same gelatin: a blended edible gelatin of medium strength. Difference in setting and melting times are due to our varying of other conditions, such as acidity. Conditions most favorable to setting (Jelly B) increase the melting time.

TABLE II

Influence of Time and Temperature upon the Maturing of Gelatin Jellies

Series No.	(All tubes stoppered after setting to prevent drying of surface film)	Setting time Minutes	Melting time (at 22.5°C.) after			
			6 hrs.	24 hrs.	48 hrs.	72 hrs.
			Min.	Min.	Min.	Min.
1.	Set at 0–1°C. Kept in ice bath for duration of experiment*	25	5	11*	13*	—
2.	Set at 0–1°C. After 60 min. Changed to 14.5°C.	25	17	74	165	220
3.	Set at 14.5°C. Kept at same temperature for duration of experiment	270	12	96	231	303

*The temperature of the bath would rise several degrees over night, which accounts for the gradual rise in melting time.

It should be of interest to test other temperatures, however, the series here presented indicates a rearrangement or orientation of the gelatin molecules which can occur at 14–15°C. but not at all or at least at an extremely slow rate, at 0°C. It is also evident that this structure is not a part of the actual solidification or gelation of the gelatin solution but an independent change for, while not actually measured it was evident to the observer that the gelatin set at 0° was very firm, notwithstanding its very low permanency at higher temperatures.

It should be of interest to observe the rate of orientation at different temperatures from 0° up to the upper limit for the setting of gelatin. Particularly would it be of interest to observe whether a jelly held at that upper limit for some period of time and then quickly set at 0°C. would show that molecular orientation had taken place.

Some of our observations included different grades of gelatin prepared so as to give jellies of approximately equal jelly strength. Typical comparisons of two such gelatins are given in Table III No. R-60 is an average strength gelatin, while M-61 is a superior gelatin. An attempt was made to prepare the jellies with such amounts of gelatin as would result in equal setting time.

TABLE III

Influence of Time on the maturing of Acidified Gelatin Jellies (pH about 3.0) prepared with Proportional Amounts of Different Grade Gelatins and kept at 14–15°C.

Series No.	Gelatin Gms.	Gelatin No.	Setting time Minutes	(Melting time at 22.5°C.) after 6 hrs.	16 hrs.	22 hrs.	48 hrs.
1.	9.6	M-61	250	16	75	120	270
2.	11.2	R-60	250	12	45	70	161

These results indicate that the stronger gelatin has a much stronger tendency towards orientation and gradual building up of a complex jelly structure than has the weaker gelatin, although the latter was used in proportionally larger amounts.

Summary

Evidence is presented which indicates that two separate processes may occur when gelatin solutions solidify:

1) Solidification, which may be quite rapid at low temperatures.

2) Orientation of molecules into an internal structure. This change is retarded by too low temperatures.

When acidified gelatin solutions are rapidly cooled to 0°C. solidification quickly occurs and orientation is largely prevented. Such a gel has little permanency at melting temperatures.

When acidified gelatin solutions are kept at 14–15°C. solidification occurs more slowly and is accompanied by molecular orientation which may continue for days, resulting in a gel with increasing resistance to melting temperatures.

To melt a gelatin requires both melting *per se* and destruction of the structure composed of linked gelatin molecules. The first of these is rapid, while at temperatures not much above the melting point the latter process is slow. ·

High-strength gelatin shows a greater tendency towards orientation of molecules than does low-strength gelatin.

THE RATE OF ADSORPTION FROM SOLUTION*

BY LLOYD E. SWEARINGEN AND BERNARD N. DICKINSON

Introduction

The rate at which adsorption equilibrium is established is an important factor in many physical, chemical and biological phenomena. The time required to attain equilibrium has been found by many experimenters to range from a few seconds up to several hours, depending on the nature of the process taking place.

In the case of gas-solid systems, the quantitative work of Bergter,[1] Giesen,[2] Harned[3] and others, as well as the older qualitative work of Kayser,[4] Travers[5] and others, indicate that adsorption equilibrium is reached rapidly, at most, usually a matter of a few minutes.

The adsorption from solutions by solid adsorbents is also characterized by high adsorption velocities. The work of Marc[6] and Arendt[7] on the adsorption of colloidal starch, albumin and gum arabic by strontium carbonate shows equilibrium to be reached in these cases in less than two minutes. On the other hand, there are numerous cases which may be cited to show the existence of much slower adsorption rates. The experiments of Lagergren,[8] Siegrist,[9] Dreyer and Douglas[10] and Schmidt[11] are typical of the many instances where the adsorption velocity has been found to be slow. The time required for equilibrium to be reached ranges from several minutes to several hours.

The objects of the experiments described in this paper are: (1) to study the rate at which adsorption takes place from true solution by different adsorbents, (2) to study the influence of the nature of the adsorbent on the rate of adsorption, (3) to determine how the nature and concentration of the adsorbate influences the rate of adsorption and (4) to determine how the rate of adsorption is influenced by the rate of stirring. The experiments were carried out with aqueous solutions of monochloracetic, dichloracetic and trichloracetic acids, using charcoal and silica gel as adsorbents.

[1] Ann. Physik, (4) **37**, 472 (1912).
[2] Ann. Physik, (4) **10**, 838 (1903).
[3] J. Am. Chem. Soc., **42**, 372 (1920).
[4] Wied. Ann., **12**, 526 (1881); **14**, 450 (1881).
[5] Proc. Roy. Soc., **78 A**, 9 (1906).
[6] Z. Elektrochemie, **20**, 515 (1914).
[7] Kolloidchem. Beihefte, **7**, 212 (1915).
[8] Bihang K. Svenska Ak. Hand., **24**, 2. Nos. 4 and 5 (1899).
[9] Dissertation, Lausanne (1910).
[10] Proc. Roy. Soc., **82B**, 168 (1910).
[11] Z. physik. Chem., **74**, 704 (1019); **77**, 646 (1911).

Experimental

Material. The silica gel used as adsorbent was prepared by the method of Patrick.[12] The hard transparent gel was crushed and screened. That portion of the gel passing a twenty-mesh but retained on a forty-mesh screen was used as adsorbent.

The charcoal used in these experiments was a blood charcoal, furnished by J. T. Baker Co. The charcoal was screened in the same manner as the gel.

The monochloracetic, dichloracetic and trichloracetic acids were obtained from the J. T. Baker Company. The monochloracetic and trichloracetic

FIG. I
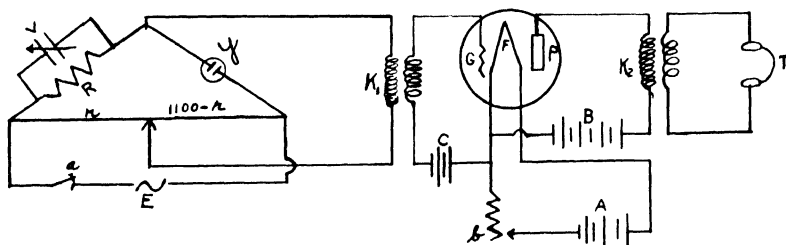
R	Resistance	A, B, C	Batteries
y	Conductivity Cell	G	Grid
V	Variable Condenser	F	Filament
r	Bridge Wire	P	Plate
a	Tap Key	K_2	Induction Cell
E	Oscillator	b	Rheostat
K_1	Induction Coil	T	Head Phones

acids gave sharp melting points, slightly below the accepted values for these substances. The dichloracetic acid was redistilled, the highest boiling fraction was collected and used.

A good grade of conductivity water was used in the preparation of the solutions. The water was boiled immediately before use to expel carbon dioxide.

Procedure. Several methods for following the adsorption were considered. Due to the rapidity and ease with which conductance measurements can be made, this method was finally selected and proved to be very satisfactory. A Wheatstone Bridge assembly with a thermionic amplifier was used to determine the resistances of the solutions. The wiring diagram is shown in Fig. 1. A pipette of about five cubic centimeters capacity with sealed-in platinized platinum electrodes was used as the conductivity cell. The cell constant was determined with 0.02 N. KCl and was frequently checked during the course of the experiments. The solution was drawn up into the cell and its resistance measured out of contact with the solid adsorbent.

To avoid the necessity of calculating concentrations by some one of the empirical equations relating conductance with concentration, it was found to be desirable to measure the conductances of the acid solutions over the ranges of concentration involved in the adsorption. By maintaining all

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[12] United States Patent 1,297,724.

variables constant in all experiments with a given acid except the concentration, the changes in concentration could be followed by changes in the position of the sliding scale. By plotting on a large scale these sliding scale readings against the known concentration of the acid, unknown concentrations corresponding to known sliding scale readings can be obtained from these curves by interpolation. These reference data and curves for the different acid solutions are given in Table I and Fig. 2.

TABLE I

Reference Data

Sliding Scale Readings for Solutions of Various Concentrations for Fixed Values of R and at 25°C

Concentration Moles per Liter	External Resistance R (ohms)	Sliding Scale Reading "r"	Concentration Moles per Liter	External Resistance R (ohms)	Sliding Scale Reading "r"
Monochloracetic Acid					
0.1120	100	593.5	0.0628	100	508.0
0.1056	100	584.5	0.0560	140	582.5
0.1004	100	577.5	0.0475	140	559.0
0.0940	100	567.5	0.0452	140	552.0
0.0886	100	559.0	0.0430	140	545.0
0.0836	100	550.0	0.0402	140	535.5
0.0793	100	542.5	0.0384	140	528.5
0.0753	100	534.0	0.0362	140	519.0
0.0716	100	526.0	0.0335	140	507.0
0.0684	100	520.0	0.0310	140	494.0
0.0655	100	512.5	0.0298	140	486.0
Dichloracetic Acid					
0.0502	40	545.0	0.0311	40	435.0
0.0471	40	529.0	0.0292	40	421.0
0.0443	40	517.5	0.0275	40	408.0
0.0423	40	505.5	0.0248	40	384.5
0.0375	40	477.0	0.0226	40	364.0
0.0359	40	468.5	0.0208	40	345.0
0.0333	40	452.0	0.0193	40	330.0
Trichloracetic Acid					
0.0512	40	691.0	0.0390	40	625.5
0.0492	40	684.0	0.0368	40	610.0
0.0468	40	671.5	0.0347	40	594.5
0.0446	40	659.5	0.0333	40	583.5
0.0426	40	648.0	0.0326	40	578.5
0.0407	40	636.0	0.0320	40	573.0

The solutions were kept at 25°C ± 0.25°C during the adsorption measurements. A stop-watch recording time to 0.2 seconds was used to time the intervals at which the conductance measurements were made.

The method used in following the concentration changes with a given acid solution may be briefly described as follows: a weighed quantity of adsorbent was placed in the adsorption flask. With the cell in position, the external resistance R and temperature were made identical with the values used in obtaining the reference data for this particular acid solution. Two
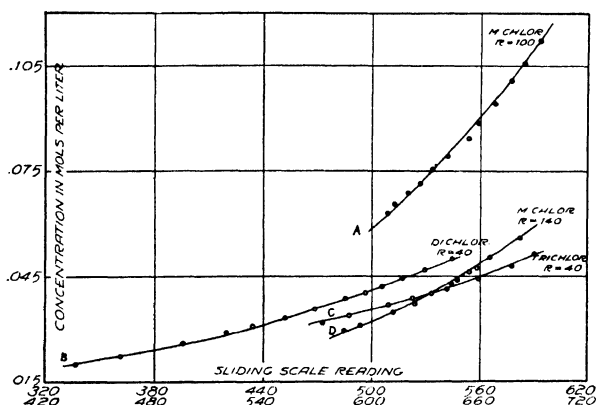
FIG. 2

Reference Curves

A.	Monochloracetic Acid	R = 100 ohms
B.	Dichloracetic Acid	R = 40 ohms
C.	Trichloracetic Acid	R = 40 ohms*
D.	Monochloracetic Acid	R = 140 ohms

* Sliding Scale Reading 100 units greater than indicated on curve.

TABLE II

The Rate of Adsorption of Monochloracetic Acid at 25°C.

Part A

Six Grams of Silica Gel with 200 c.c. of 0.1 N. Acid

External Resistance R = 100 Ohms

Series No. 1 (Continuous Agitation)

Time in Seconds	Bridge Reading	Concentration Moles per Liter	Adsorption Moles per Liter	Adsorption, Moles per Gram Adsorbent	Adsorption Velocity Constant
t	r	C	X	X/M	k
0	577.0	0.1000	0.0000	0.0000	—
5	568.5	0.0946	0.0054	0.0009	0.0112
10	561.0	0.0898	0.0102	0.0017	0.0107
15	549.5	0.0831	0.0169	0.0028	0.0123
20	542.5	0.0794	0.0206	0.0034	0.0115
30	530.0	0.0730	0.0270	0.0045	0.0105
45	521.5	0.0690	0.0310	0.0054	0.0082
60	516.5	0.0668	0.0332	0.0055	0.0067
75	514.5	0.0660	0.0340	0.0056	—
90	514.0	0.0658	0.0342	0.0057	—

TABLE II (Continued)

Series No. 2.   (Intermittent Agitation)

0	577.0	0.1000	0.0000	0.0000	—
15	550.0	0.0834	0.0166	0.0027	—
60	537.5	0.0768	0.0332	0.0039	—
105	530.0	0.0731	0.0269	0.0045	—
150	524.5	0.0704	0.0296	0.0049	—
210	520.5	0.0686	0.0314	0.0052	—
315	516.0	0.0666	0.0334	0.0055	—
450	514.5	0.0660	0.0340	0.0056	—
720	514.0	0.0657	0.0343	0.0057	—
900	514.0	0.0657	0.0343	0.0057	—

Part B

Ten Grams of Blood Charcoal with 200 c.c. of 0.1 N. Acid
External Resistance R 100 Ohms.   (Continuous Agitation)

t	r	C	X	X/M	k
0	577.5	0.1000	0.0000	0.0000	—
10	573.0	0.0970	0.0030	0.0003	0.0030
15	569.5	0.0948	0.0062	0.0006	0.0035
20	567.5	0.0938	0.0072	0.0007	0.0032
30	563.5	0.0913	0.0097	0.0009	0.0030
45	556.5	0.0869	0.0131	0.0013	0.0031
60	555.0	0.0860	0.0140	0.0014	0.0025
90	550.5	0.0836	0.0164	0.0016	0.0020
120	549.5	0.0832	0.0168	0.0017	—
210	548.0	0.0824	0.0176	0.0017	—
300	547.5	0.0820	0.0180	0.0018	—
420	546.5	0.0816	0.0184	0.0018	—
600	546.0	0.0812	0.0188	0.0019	—
900	545.5	0.0810	0.0190	0.0019	—

Part C

Six Grams of Silica Gel with 200 c.c. of 0.048 N. Acid
External Resistance R = 140 Ohms.

Series No. 1. (Continuous Agitation)

0	560.0	0.0480	0.0000	0.0000	—
5	551.5	0.0452	0.0028	0.0004	0.0116
10	545.0	0.0430	0.0050	0.0008	0.0110
15	537.5	0.0409	0.0071	0.0012	0.0107
20	527.5	0.0382	0.0098	0.0016	0.0115
30	508.0	0.0339	0.0141	0.0023	0.0116
45	500.0	0.0322	0.0158	0.0026	0.0089
60	492.0	0.0309	0.0171	0.0028	0.0073
75	491.5	0.0307	0.0173	0.0029	—
90	491.0	0.0306	0.0174	0.0029	—

TABLE II (Continued)

Series No. 2. (No Agitation)

t	r	C	X	X/M	k
0	560.0	0.0480	0.0000	0.0000	—
15	537.5	0.0409	0.0071	0.0012	—
45	527.0	0.0381	0.0099	0.0016	—
65	518.0	0.0360	0.0120	0.0020	—
110	504.5	0.0331	0.0149	0.0025	—
170	501.5	0.0325	0.0155	0.0026	—
240	497.0	0.0316	0.0164	0.0027	—
320	493.0	0.0310	0.0170	0.0028	—
720	491.5	0.0307	0.0173	0.0029	—

Part D

Ten Grams of Blood Charcoal with 200 c.c. of 0.0502 N. Acid
External Resistance R = 140 Ohms. (Continuous Agitation)

t	r	C	X	X/M	k
0	567.0	0.0502	0.0000	0.0000	
10	562.5	0.0487	0.0015	0.0001	0.0030
15	560.0	0.0480	0.0022	0.0002	0.0030
20	558.0	0.0472	0.0030	0.0003	0.0031
30	554.0	0.0460	0.0042	0.0004	0.0029
50	550.0	0.0446	0.0056	0.0005	0.0031
60	547.0	0.0438	0.0064	0.0006	0.0023
90	544.5	0.0430	0.0072	0.0007	0.0012
150	543.0	0.0425	0.0077	0.0008	—
240	540.5	0.0418	0.0084	0.0008	—
390	537.5	0.0409	0.0093	0.0009	—
675	534.5	0.0400	0.0102	0.0010	—
915	534.5	0.0400	0.0102	0.0010	—

hundred cubic centimeters of the acid solution of known concentration, previously brought to 25°C. was added to the adsorption flask. The stop watch was started at the half-hour point. Immediately, a sample was drawn into the pipette and the sliding scale adjusted to the minimum sound point and a reading taken. The solution in the pipette was then returned to the adsorption flask and this operation repeated at frequent intervals. The time of each sliding scale reading was taken at the half-fill time for the pipette. From the sliding scale readings thus obtained, the corresponding concentrations could be read from the reference curves for this particular acid. The adsorbed acid is expressed in terms of moles per gram of adsorbent.

To determine the influence of agitation on the rate at which solute was removed from solution, two series of experiments were conducted with silica gel. In Series No. 1, the solution and adsorbent were vigorously shaken during the entire course of the experiment. In Series No. 2, the solution and adsorbent were shaken only for a few seconds immediately before samples were withdrawn. The first procedure was applied to all of the samples in which charcoal was used as an adsorbent. Results obtained under the same experimental conditions were markedly consistent.

TABLE III

The Rate of Adsorption of Dichloracetic Acid at 20°C

Part A

Six Grams of Silica Gel and 200 c.c. of 0.0502 N. Acid
External Resistance R = Ohms

Series No. 1.   (Continuous Agitation)

Time in Seconds	Bridge Reading	Concentration Moles per Liter	Adsorption Moles per Liter	Adsorption, Moles per Gram Adsorbent	Adsorption Velocity Constant
t	r	C	X	X/M	k
0	544.5	0.0502	0.0000	0.0000	—
5	534.0	0.0482	0.0020	0.0003	0.0081
10	526.0	0.0462	0.0040	0.0006	0.0082
15	517.5	0.0444	0.0058	0.0009	0.0082
20	508.5	0.0426	0.0076	0.0012	0.0082
30	490.0	0.0395	0.0107	0.0018	0.0080
45	460.0	0.0346	0.0156	0.0026	0.0082
60	434.5	0.0307	0.0195	0.0032	0.0082
75	418.5	0.0289	0.0213	0.0035	0.0074
90	408.0	0.0276	0.0226	0.0037	0.0066
120	398.5	0.0265	0.0237	0.0039	—
150	394.5	0.0260	0.0242	0.0040	—

Series No. 2.   (Intermittent Agitation)

Time in Seconds	Bridge Reading	Concentration Moles per Liter	Adsorption Moles per Liter	Adsorption, Moles per Gram Adsorbent	Adsorption Velocity Constant
0	544.5	0.0502	0.0000	0.0000	—
15	517.5	0.0444	0.0058	0.0009	—
55	503.5	0.0417	0.0085	0.0014	—
100	490.5	0.0395	0.0107	0.0018	—
165	472.0	0.0363	0.0139	0.0023	—
225	459.5	0.0345	0.0157	0.0026	—
285	449.5	0.0331	0.0171	0.0028	—
360	437.5	0.0314	0.0188	0.0032	—
460	429.5	0.0303	0.0199	0.0033	—
540	422.0	0.0294	0.0208	0.0034	—
690	411.5	0.0281	0.0221	0.0037	—
840	404.5	0.0272	0.0232	0.0038	—
1020	398.0	0.0264	0.0238	0.0039	—
1240	394.5	0.0260	0.0242	0.0040	—
1560	390.5	0.0256	0.0246	0.0041	—
1800	390.0	0.0255	0.0247	0.0041	—

TABLE III (Continued)

Part B

Ten Grams of Blood Charcoal with 200 c.c. of 0.0502 N. Acid
External Resistance R = 40 Ohms. (Continuous Agitation)

t	r	C	X	X/M	k
0	544.0	0.0502	0.0000	0.0000	—
10	533.0	0.0481	0.0021	0.0002	0.0043
20	525.0	0.0461	0.0041	0.0004	0.0043
30	517.5	0.0444	0.0058	0.0006	0.0041
45	500.5	0.0413	0.0089	0.0009	0.0043
60	489.5	0.0393	0.0109	0.0011	0.0041
75	473.0	0.0366	0.0136	0.0014	0.0042
90	462.5	0.0350	0.0152	0.0015	0.0040
120	449.0	0.0330	0.0172	0.0017	0.0035
180	441.5	0.0320	0.0182	0.0018	—
360	427.0	0.0300	0.0202	0.0020	—
800	411.5	0.0281	0.0221	0.0022	—
1500	404.5	0.0272	0.0230	0.0023	—
2400	400.5	0.0267	0.0235	0.0023	—

TABLE IV

The Rate of Adsorption of Trichloracetic Acid at 25°C

Part A

Six Grams of Silica Gel with 200 c.c. of 0.0505 N. Acid
External Resistance R = 40 Ohms

Series No. 1 (Continuous Agitation)

Time in Seconds	Bridge Reading	Concentration Moles per Liter	Adsorption Moles per Liter	Adsorption Moles per Gram Adsorbent	Adsorption Velocity Constant
t	r	C	X	X/M	k
0	688.5	0.0505	0.0000	0.0000	—
5	684.0	0.0493	0.0012	0.0002	0.0048
10	679.5	0.0482	0.0023	0.0004	0.0047
15	673.0	0.0470	0.0035	0.0006	0.0048
20	667.0	0.0459	0.0046	0.0007	0.0048
30	655.0	0.0438	0.0067	0.0011	0.0047
45	636.5	0.0408	0.0097	0.0016	0.0047
60	625.0	0.0390	0.0115	0.0019	0.0043
75	615.0	0.0375	0.0130	0.0022	0.0040
90	606.5	0.0363	0.0142	0.0024	—
120	604.0	0.0360	0.0145	0.0024	—

TABLE IV (Continued)

Series No. 2. (Intermittent Agitation)

0	688.5	0.0505	0.0000	0.0000	—
20	677.0	0.0459	0.0046	0.0007	—
65	653.5	0.0436	0.0069	0.0011	—
120	641.5	0.0416	0.0089	0.0015	—
180	630.5	0.0399	0.0106	0.0018	—
240	623.5	0.0388	0.0117	0.0019	—
340	616.5	0.0377	0.0128	0.0021	—
420	612.5	0.0372	0.0133	0.0022	—
540	609.5	0.0367	0.0138	0.0023	—
720	605.0	0.0361	0.0144	0.0026	—
900	603.5	0.0359	0.0146	0.0026	—
1200	603.0	0.0358	0.0147	0.0027	—

Part B

Ten Grams of Blood Charcoal to 200 c.c. of 0.0512 N. Acid
External Resistance R = 40 Ohms. (Continuous Agitation)

t	r	C	X	X/M	k
0	691.5	0.0512	0.0000	0.0000	
10	680.5	0.0486	0.0026	0.0003	0.0052
15	675.0	0.0474	0.0038	0.0004	0.0051
20	668.5	0.0462	0.0050	0.0005	0.0051
30	657.0	0.0441	0.0071	0.0007	0.0050
45	635.0	0.0406	0.0106	0.0011	0.0052
60	616.5	0.0377	0.0135	0.0013	0.0051
75	608.5	0.0366	0.0146	0.0014	0.0045
90	607.0	0.0364	0.0148	0.0015	0.0038
120	605.5	0.0362	0.0150	0.0015	—
300	604.0	0.0360	0.0152	0.0015	—
900	602.5	0.0358	0.0154	0.0015	—
1200	601.0	0.0356	0.0156	0.0016	—
2405	589.5	0.0341	0.0171	0.0017	—

Discussion of Results

It is natural to expect the initial adsorption rate to be proportional to the concentration of the adsorbate. A rate equation of the form $\frac{dx}{dt} = k(C - X)$ should hold when the rate is directly proportional to the concentration of the adsorbate. The solution of this differential equation is (1) $X = C(1-e^{-kt})$, where X is the amount adsorbed in moles; C, the equilibrium concentration in moles per liter; t, time in seconds; k, a constant and e, the natural logarithm base. The range over which this equation expresses the experimental data can be determined by the constancy of the k member. The numerical values of k have been calculated for several time intervals in each experi-

ment. The values calculated appear in the right hand column of each table. The k values show considerable constancy in the early part of each experiment, when the solutions are vigorously agitated. Up to the time at which the k values begin to seriously fluctuate, 75 to 80% of the total amount of material adsorbed has been removed.

Since the equilibrium is a dynamic one, it should be possible to modify this equation to take care of the backward diffusion of the solute from the
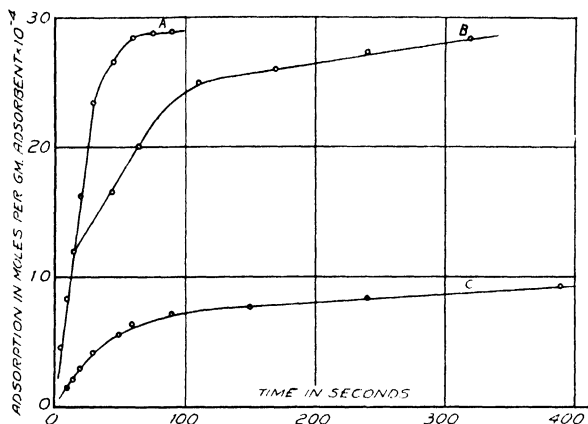
FIG. 3

Rate of Adsorption from 0.1N Monochloracetic Acid
A.   Adsorbent, Silica Gel. Series No. 1
B.   Adsorbent, Silica Gel. Series No. 2
C.   Adsorbent, Charcoal

adsorbent into solution. This modified equation should express the rate for the entire process. Any modification made must be negligible until the process is from 75 to 80% complete. If it is assumed that diffusion from the adsorbent is proportional to the amount adsorbed raised to some power, then the rate would be expressed by an equation of the sort (2) $\dfrac{dX}{dt} = k(C - X) - KX^n$.

This equation gives Freundlich's equation as a boundary condition, as when dX/dt is zero, then $k(C - X) = KX^n$. The series solution of this equation is so slowly convergent that a great number of terms must be considered. The agreement of this solution with the equation with the experimental results was not good enough to justify its application.

When the system is not shaken, the rate is largely dependent on the time required for the solute to diffuse into the depleted regions in the neighborhood of the adsorbent. The initial rate is the same in the continuously and intermittantly agitated samples. In a short time the solute has been largely removed from the solution immediately surrounding the adsorbent, and in those samples not continuously agitated, there is a marked decrease in adsorption rate. With the continuously agitated gel-acid samples, equilibrium is reached in from 1.5 to 2.5 minutes in all cases. With the intermittently agitated samples, from 12 to 30 minutes are required for equilibrium to be
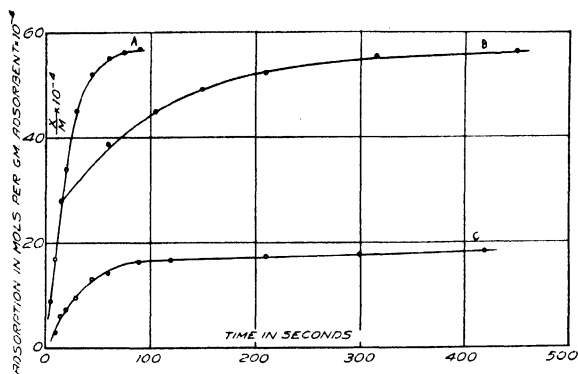
FIG. 4

Rate of Adsorption from 0.05 N Monochloracetic Acid
A. Adsorbent, Silica Gel. Series No. 1
B. Adsorbent, Silica Gel. Series No. 2
C. Adsorbent, Charcoal

reached. With charcoal the rate of adsorption is considerably slower than with the gel and in some cases, long periods of time are required to reach the final stages of the equilibrium.

From Figs. 3, 4, 5 and 6, it is seen that the silica gel and charcoal adsorb the acids at markedly different rates. The gel adsorbs all of the acids much faster than the charcoal. Only in the case of the trichloracetic acid does the charcoal adsorb acid at a rate approaching that of the gel. The gel adsorbs a greater total quantity of each acid than the charcoal.
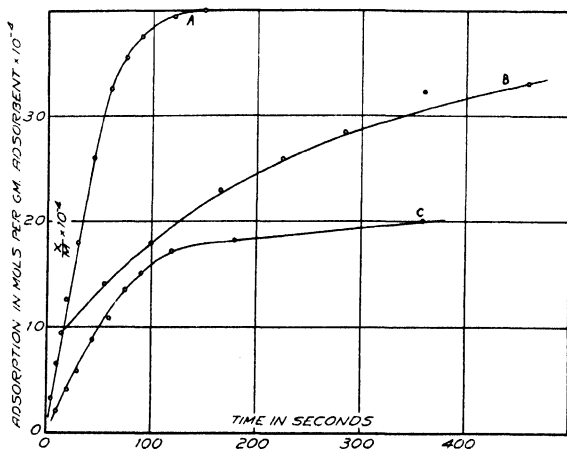
FIG. 5

Rate of Adsorption from 0.05 N Dichloracetic Acid.
A. Adsorbent, Silica Gel. Series No. 1
B. Adsorbent, Silica Gel. Series No. 2
C. Adsorbent, Charcoal

The different acids are adsorbed by each adsorbent at different rates. From Figs. 4, 5 and 6, it is seen that the early rate order for the gel is mono- > di- > tri- while with the charcoal the early rate order is reversed to tri- > di- > mono-.

A comparison of the amounts of monochloracetic acid removed at equal times from the two acid concentrations shows the rate to be dependent on the concentration of the acid. In 50 seconds, practically twice (1.92) as much
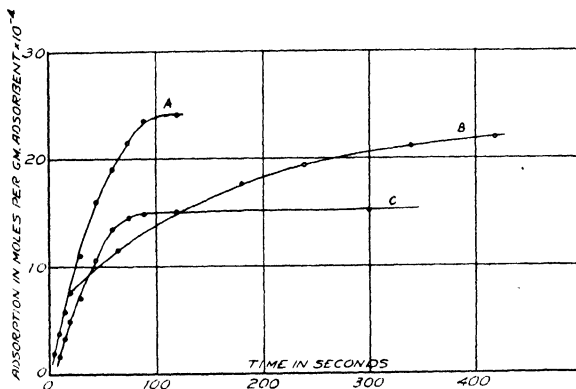
Fig. 6

Rate of Adsorption from 0.05 N Trichloracetic Acid
    A.   Adsorbent, Silica Gel. Series No. 1
    B.   Adsorbent, Silica Gel. Series No. 2
    C.   Adsorbent, Charcoal

monochloracetic acid has been removed from the 0.1 N solution as has been removed from the 0.048 N acid solution. With charcoal, 2.4 times more acid has been removed from the 0.1 N than from the 0.048 N acid at both the 50 and the 100 second point.

Summary

The rates of adsorption of monochloracetic, dichloracetic and trichloracetic acid by silica gel and blood charcoal have been measured. The adsorption was followed by an electrical conductance method.

The results indicate that with vigorous agitation, from 75 to 80% of the adsorption takes place in such manner as to be directly proportional to the concentration of the solute. The rate of adsorption and the time required for establishing equilibrium are markedly dependent on the amount of agitation, the nature of the solute, the concentration of the solute, the nature of the adsorbent, and the amount of agitation.

Norman, Oklahoma.

COAGULATION OF PROTEINS IN MARINE BORERS

BY WILDER D. BANCROFT

My attention has been drawn to a paper by L. F. Shackell,[1] entitled "Studies in Protoplasm Poisoning" and published in 1923. Mr. Shackell has anticipated by nearly eight years some of the conclusions in regard to disinfection drawn by Bancroft and Richter.[2] His paper seems to me so important and has attracted so little attention hitherto that I am reproducing selected paragraphs.

"In the course of an extended investigation into the protection of wood from the attacks of marine borers,[3] opportunity has been afforded the writer to carry on a systematic study of the changes in protoplasm produced by poisons. The major part of this paper is concerned with observations on 8,000 specimens of the small crustacean borer, *Limnoria lignorium*. For the sake of comparison in one phase of this study, results with 7500 specimens of a fresh-water cyprid and with about 1,500 specimens of the brine shrimp, *Artemia*, from Great Salt Lake have also been included. The data were collected during the summers of 1916, 1917, 1921, and 1922.

"*Limnoria* possesses a number of advantages for an investigation of the present type. It occurs in countless numbers in untreated wooden structures standing in the sea water of the Atlantic, Pacific, and Gulf coasts. It is a small marine isopod 2 to 3 mm. long and 1 to 1.5 mm. wide. It may be readily picked up in a drop of water by means of a pipette or medicine dropper.

"When it is transferred to sea water from wood in which it is burrowing, and on which it probably subsists, *Limnoria* keeps in constant motion by means of numerous legs and swimmers. This continuous activity makes it possible to distinguish sharply the moment at which complete bodily paralysis has been induced by a poison [phenol, o-cresol, m-cresol, p-cresol, pyrocatechin, resorcinol, hydroquinone, or pyrogallol]. Again the first spontaneous movement of the animal after its removal from the toxic solution may be used to delimit a certain stage in its recovery.

"Poisoning has been looked upon by the majority of workers in this field as essentially chemical in nature. A number in fact have attempted to apply the monomolecular formula to the killing of bacteria and other organisms. The reader who is interested in this phase of the subject will find good bibliographies in the paper by Bowers,[4] Brooks[5] and Fairhall.[6] The protest voiced by Brooks against the stereotyped application of the monomolecular formula

[1] J. Gen. Physiol., **5**, 783 (1923).

[2] J. Phys. Chem., **35**, 511 (1931).

[3] Shackell: Proc. Am. Wood Preservers' Assn., **1915**, 233; **1916**, 124; Teasdale and Shackell: Engineering News Record, **1917**, Nov. 1.

[4] Illinois Biological Monographs, **4**, 127 (1917).

[5] J. Gen. Physiol., **1**, 61 (1918).

[6] Mil. Surg., **1**, 295 (1922).

is particularly timely. A similar stand has been taken by Rideal and Rideal.[1] The writer believes that the time is ripe[2] for a re-orientation with respect to chemical and physical explanations of phenomena peculiar to living matter.

"The writer is of the opinion that only by taking into consideration such factors as cell permeability, osmosis, surface tension and adsorption, viscosity, electrical double layers, distribution coefficients between lipins and water, swelling, coalescence, and dispersion, in addition to factors which are unquestionably chemical in nature, can poisoning be adequately described. Nevertheless, in considering the possible mechanisms of poisoning by phenols, there are two of these factors on which attention may be focussed for the time being. These are: (1) the distribution of a phenol between the water and lipins of protoplasm [Meyer-Overton]; and (2) the aggregation or coalescence of protein particles [Claude Bernard]. In this connection it is worth noting that the monohydroxyphenols—carbolic acid and the cresols—are more soluble in many substances of lipoid character than they are in water, and that an increase in the number of hydroxyl groups in the phenols is accompanied by increased solubility in water. Furthermore, carbolic acid and the cresols are more powerful flocculants of proteins than the di- or trioxyphenols. The latter, however, are more easily oxidized and disintoxicated [detoxicated?] than the monoxyphenols. A further fact bearing on the above points which was seen regularly in the writer's experiments, was that in dead animals the tissues were quite opaque—in marked contrast to the translucency seen in the tissues of living animals. This seems to indicate that death is determined by a certain grade of aggregation of the cell proteins.

"As a working concept of the general lipin-protein relationship in unpoisoned protoplasm, let it be assumed that a factor in the maintenance of the normal dispersity of tissue proteins is the adsorption of ultramicroscopic lipins at protein-water interfaces. Now let a phenol, which is relatively slightly soluble in water, but quite soluble in lipins—such as carbolic acid or one of the cresols—diffuse from its aqueous solution into the tissue. The accumulation of the phenol in the lipoid adsorption layer, which may reach a concentration several times that in the water must at least disturb the pre-existing lipin-protein relationship.[3] This disturbance will conceivably facilitate the aggregation (flocculation) of the tissue proteins.

"The above theory of poisoning assumes, in short, that as soon as a phenol penetrates into tissue cells, pathologic aggregation of the cell proteins is initiated. Of the factors which influence the rate at which this aggregation proceeds, two may be mentioned. These factors, which are themselves conditioned by the special chemical and physical characteristics of the particular phenol, are first, the rate at which the phenol is taken up by the tissue lipins; and second, the rate at which the phenol is chemically disintoxicated. When

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[1] "Disinfection," 299 (1922).

[2] [This was a bad guess; but the time is now ripe.]

[3] [This may be what Clowes means by the statement that anaesthesia is the disturbance of a complex equilibrium.]

coalescence of the protein particles has reached a stage where the redispersion is impossible, the protoplasm may be said to be dead.

"The concept of an irreversible aggregation of cellular proteins, as the determinant of death of poisoned cells, may not be the major factor in senescence and in death from so-called natural causes. Some preliminary observations with *Limnoria* made by the writer indicate that in poisoning of a severe or fatal grade there is a catalysis of senescence. A similar view was advanced some years ago by Osterhout.[1] The same investigator[2] has pointed out that the resistance of all the cells is lowered permanently by poisoning of any severity. The observations of the writer tend to confirm this view. Further work along this line is in progress."

As will be seen from these quotations, Mr. Shackell was quite clear on reversible and irreversible aggregation of tissue proteins. He seems not to have drawn the apparently obvious corollary that a peptizing agent for proteins, sodium rhodanate for instance, should bring *Limnoria* out of paralysis if applied subsequent to the phenol, and should prevent the reversible aggregation if the sodium rhodanate is administered before the phenol. It is to be hoped that somebody will confirm this prediction experimentally.

Cornell University.

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[1] Science, **39**, 544 (1914).

[2] "Monographs on Experimental Biology" (1922).

THE PROMOTING ACTION OF COPPER SULFIDE ON THE SPEED OF PRECIPITATION OF ZINC SULFIDE

(The So-called Coprecipitation of Zinc with Copper Sulfide)

BY I. M. KOLTHOFF AND E. A. PEARSON[1]

Introduction

The "carrying down" of zinc sulfide by copper sulfide when the latter is precipitated by hydrogen sulfide at an acidity such that the zinc solution does not react with the precipitant has been known for a long time. The phenomenon has been called vaguely "induced precipitation" and has been a subject of considerable dispute as to its extent and nature. Rivot and Bouquet[2] as well as Calvert[3] claimed that the separation of copper and zinc in acid medium does not yield accurate results as some zinc is found in the copper sulfide. Spirgatus[4] on the other hand recommended the method provided that the copper sulfide were precipitated from strongly acid medium; whereas Grundmann[5] advocated a double precipitation. This was confirmed by Fresenius (comp. Grundmann[5]) and by Baubigny.[6] The latter made extensive studies and found that even in acid medium, copper sulfide has a tendency to carry down metals of the third group of the qualitative system. At the suggestion of Fresenius, Larsen[7] made a practical study of the separation of copper and zinc and concluded that good results were obtained if the precipitation were made from relatively strong acid medium, the copper sulfide filtered immediately after the precipitation and washed with 0.5 N hydrochloric acid containing little hydrogen sulfide followed by dilute hydrogen sulfide alone. The copper sulfide was zinc free. Berglund,[8] in a more accurate investigation, was able to confirm Larsen's results. Glixelli[9] was the first to attack the carrying down of zinc by copper sulfide in a more general way and gave in an excellent paper a clear statement of the facts. From the known solubility product of zinc sulfide, he calculated that in dilute zinc solutions, zinc sulfide should precipitate with hydrogen sulfide even at an acidity as high as 1 N. This he showed to be true; however, months were required for the precipitation to occur, this time being called period of induction. Kolthoff and van Dyk[10]

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[1] From a thesis submitted by E. A. Pearson to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Rivot and Bouquet: J. prakt. Chem., 51, 203 (1851).

[3] Calvert: J. prakt. Chem., 71, 155 (1855).

[4] Spirgatus: J. prakt. Chem., 57, 184 (1852).

[5] Grundmann: J. prakt. Chem., 73, 241 (1858).

[6] Baubigny: Compt. rend., 94, 1183, 1251, 1473, 1595 (1882); 95, 34 (1883); 105, 751, 805 (1888); 107, 1148 (1888); 108, 236, 450 (1889).

[7] Larsen: Z. anal. Chem., 17, 312 (1878).

[8] Berglund: Z. anal. Chem., 22, 184 (1883).

[9] Glixelli: Z. anorg. Chem., 65, 297 (1907).

[10] Kolthoff and van Dyk: Pharm. Weekblad, 59, 1351 (1922).

showed that the latter is proportional to the square of the hydrogen ion concentration and inversely proportional to the zinc ion concentration. From a study of S. Krishnamurti[11] on the speed of precipitation of cadmium sulfide it follows that activities should be read here instead of concentrations. In the case of zinc sulfide, the induction period decreases with increasing temperature (Kolthoff and van Dyk). Glixelli showed that the precipitation of zinc sulfide is an autocatalytic process; not only solid zinc sulfide but also copper sulfide and cadmium sulfide promote the precipitation of zinc sulfide in acid medium by hydrogen sulfide. Kolthoff and van Dyk[10] from a great number of experiments concluded that no zinc is precipitated with copper sulfide if hydrogen sulfide is passed through the equimolecular copper-zinc sulfate mixture at room temperature at an acidity of at least 0.5 N sulfuric or hydrochloric acid. The filtration has to be made immediately after the precipitation of the copper as on longer standing zinc appears to be present in the copper sulfide. If the precipitation were carried out under the above conditions in a boiling solution, 1 to 2% zinc was found in the filtrate. Therefore, if the precipitation is made at higher temperature, a higher acidity is required than at room temperature. This work was confirmed by W. Böttger and Druschke.[12]

So far only experimental facts have been described. In recent years the interpretation of the facts observed in the promoted precipitation of metals of the third group by hydrogen sulfide in the presence of metals of the second group has been the subject of many investigations and theories. It is emphasized that in the following discussion we confine ourselves to the copper-zinc problem only; other combinations will be studied more systematically in the future.

K. Scheringa[13] advanced the peculiar interpretation that zinc sulfate (not zinc sulfide) forms a solid solution with copper sulfide, the former being distributed between solution and precipitate according to the partition law. In a later paper,[14] however, he is doubtful whether his experimental work has been correct and he rejects his statement without contributing anything new to the problem. In the work described in the present paper, it is definitely shown that zinc sulfide neither forms a solid solution in copper sulfide nor is it adsorbed by the latter.

In agreement with Glixelli,[9] Kolthoff and van Dyk[10] concluded that copper sulfide promotes the precipitation of zinc sulfide. Their paper is mainly of practical character, though they state[15] that "in acid medium zinc sulfide is extremely slightly soluble and that it is not surprising that copper sulfide promotes the precipitation of zinc sulfide." Böttger and Druschke[12] concluded that zinc sulfide is coprecipitated with copper sulfide, but their experimental data show definitely that the speed of precipitation of zinc sulfide is increased in presence of copper sulfide. They also found that on long treatment of the copper sulfide containing some zinc sulfide with 1 N hydrochloric acid all the

[11] S. Krishnamurti: J. Chem. Soc., **1926**, 1549.

[12] Böttger and Druschke: Ann., **453**, 315 (1927).

[13] K. Scheringa: Pharm. Weekblad, **55**, 431 (1918).

[14] K. Scheringa: Pharm. Weekblad, [57, 1294 (1920).

[15] Pharm. Weekblad, **59**, 1353 (1922).

zinc could be extracted from the precipitate. This is in harmony with our results, but contrary to the statements of D. Balarew.[16] In recent years, the latter has contributed interesting data to the problem of coprecipitation. He claims that the carrying down of zinc sulfide by copper sulfide is explained by his theory of "inner adsorption." The "coprecipitation" should be entirely a capillary phenomenon like the coprecipitation of potassium permanganate and other salts with barium sulfate. It will be shown below that the carrying down of zinc sulfide by copper sulfide is not a coprecipitation. Balarew's experimental work seems to be of doubtful character as he was unable to extract zinc sulfide from copper sulfide even with concentrated hydrochloric acid, whereas neither Böttger and Druschke[12] nor the present authors experienced particular difficulties in extracting the zinc from the precipitate.

F. Feigl[17] attempted to clear up the entire problem of the carrying down of sulfides of group three with those of group two by his co-ordination theory. He rejects the ionic theory and the law of mass action insofar as the precipitation of sulfides is concerned and proposes the idea that the residual valence of the sulfur in the sulfides may lead to the following types of co-ordination compounds (hence Feigl assumes a coprecipitation to take place):

1. $MS - SH_2$ Hydrosulfide
2. $MS - S$ Polysulfide
3. $M_1S - SM_1$ Isopolymer—ordinary sulfide, polymerized
4. $M_1S - SM_2$ Heteropolymer—mixed sulfide

The Cu-Zn case then is represented by type 4.

This theory and the experimental evidence has been vigorously attacked by O. Ruff and Hirsch.[18] In their studies of fractional precipitation these investigators[19] had found that the mass action law (and the solubility product principle) are the decisive factors in separations and that occlusions, adsorption or mixed crystal formation are of minor importance. In polemical papers, Feigl[20] as well as Ruff[21] defended their antagonistic view points without changing any of their former statements. Feigl in his generalization is undoubtedly wrong as will be shown in this paper on the Cu-Zn combination. It must be admitted, however, that Ruff and Hirsch are not entirely clear and consistent as may be inferred from a few citations from their interesting papers: "Die scheinbaren Wiedersprüche zum Massenwirkungsgesetze welche den Anlass zur Aufstellung der Hypothese von der Bildung komplexer Sulfide gegeben hatten (Feigl), haben sich auf die Anwendung falscher Zahlen und Begriffe zurückführen lassen."[22] Still, in a later paper,[23] Ruff claims that zinc

[16] D. Balarew: Z. anorg. allgem. Chem., **165**, 192 (1927); Kolloidchem. Beihefte, **30**, 249 (1930). The latter paper gives a complete review of Balarew's work on inner adsorption.

[17] F. Feigl: Z. anal. Chem., **65**, 25 (1924).

[18] Ruff and Hirsch: Z. anorg. allgem. Chem., **151**, 81 (1925).

[19] Ruff and Hirsch: Z. anorg. allgem. Chem., **146**, 388 (1925); **150**, 84 (1926).

[20] Feigl: Z. anorg. allgem. Chem., **157**, 251, 269 (1926).

[21] O. Ruff and B. Hirsch: Z. anorg. allgem. Chem., **151**, 81 (1926); O. Ruff and E. Ascher: **185**, 369 (1929); Ruff: **185**, 387 (1929).

[22] Z. anorg. allgem. Chem., **151**, 95 (1926).

[23] Z. anorg. allgem. Chem., **185**, 395 (1929).

sulfide can be coprecipitated with copper sulfide in the presence of an excess of hydrogen sulfide or sulfide. By molecular attraction between copper sulfide and zinc sulfide a kind of mixed crystal can be formed: "Die sogenannten induzierten Fällungen lassen sich in der Hauptsache auf Veränderung der primären Sulfide, d. h. die Anlagerung oder Adsorption von Schwefelwasserstoff an diesen oder auf die Bildung einer undurchlassigen Hülle aus dem primären Sulfid mit dem kleineren Löslichkeitsprodukte und das sekundäre mit dem grösseren zurückführen und so befriedigend erklären."[24]

In rejecting the applicability of the mass action law, Feigl overlooks one important factor, namely, that it can be applied only in the state of equilibrium. Therefore, his objections to the failure of this law cannot be accepted. It is a well-known fact that the precipitation of the metals of the third group by hydrogen sulfide in relatively weakly acid medium is a slow process. At the beginning of this paper, this "induction period" for zinc sulfide has already been mentioned. The velocity of the zinc sulfide formation in acid medium is small as the concentration of one of the reacting ions (sulfide ion) is extremely small. Therefore, in studying the precipitation of the metals of the third group in presence of those of the second group by hydrogen sulfide, it would be a great mistake to predict and explain the facts on the basis of the ratios of the solubility products. The latter principle can be applied only when the two stable solid phases are in equilibrium.

The authors have made an extensive study of the so-called coprecipitation of zinc sulfide with copper sulfide and have arrived at the conclusion that there is here neither a coprecipitation nor a mixed crystal formation. Whether this conclusion holds for all other metal combinations seems doubtful considering the various facts described in the literature (cf. esp. Baubigny,[6] Feigl;[17,20] Ruff and Hirsch[18,19,21] and Böttger and Druschke[12]); this subject will be a problem of further study.

That our interpretation of the copper-zinc hydrogen sulfide behavior is of primary importance for other combinations as well, is without question, considering its general character. It is rather peculiar that the precipitation of zinc sulfide in acid medium in the presence of copper sulfide is usually interpreted as a coprecipitation or mixed crystal formation. A simple statement of the facts observed reveals immediately that neither of the two "explanations" is correct. If a mixture of copper and zinc sulfate is treated at room temperature in about 0.36 N sulfuric acid with hydrogen sulfide and filtered immediately after the quantitative precipitation of the copper all zinc is found in the filtrate. If the mixture is allowed to stand before filtration, some zinc separates on the precipitate as zinc sulfide, its amount increasing with time. From the fact that in the first stage only copper sulfide is precipitated can be inferred that there is neither a coprecipitation nor an adsorption. . The copper sulfide promotes (induces) the precipitation of zinc from its supersaturated solutions and the problem, therefore, is reduced to the following question: Why is it that the precipitation of zinc sulfide is favored by the presence of copper sulfide? In answering this problem two points were con-

[24] Z. anorg. allgem. Chem., 151, 95 (1926).

sidered to be of primary importance: a. Copper sulfide as other sulfides adsorbs hydrogen sulfide, or sulfide ions at its surface (see also experimental part); therefore, the concentration of the reacting ion ($S^=$) will be greater at the surface of the sulfide than in the bulk of the solution. Since the velocity of formation of zinc sulfide in the solution is relatively small it may be expected that its formation will be accelerated at the surface of copper sulfide. This interpretation was confirmed by experiments in which adsorbed hydrogen sulfide or part of it was replaced by organic compounds containing polar sulfur. The promoting effect of copper sulfide on the precipitation of zinc sulfide was inhibited by this decrease of the adsorbed hydrogen sulfide. b. Copper sulfide like all finely divided substances, will favor the separation of a substance from its supersaturated solution; the surface acts as a center of crystallization or nucleus formation. If this interpretation were right, it could be expected that copper sulfide does not exert a specific inducing effect upon the precipitation of zinc sulfide from acid medium, but that other finely divided substances like barium sulfate, alumina, charcoal, talcum, silica, filter paper, etc., would show a similar effect. Some of these experiments have already been made by Glixelli; in the experimental part of this paper, quite a few substances are mentioned which qualitatively exert the same influence upon the precipitation of zinc sulfide as copper sulfide does.

Experimental Part

Materials used: *Copper sulfate* penta hydrate was obtained in a pure state by recrystallizing a C.P. product three times from water, traces of ferrous iron being removed in the first crystallization by oxidation with bromine water. The salt was kept in a desiccator over deliquescent sodium bromide. Qualitative and quantitative tests indicated its purity.

Zinc sulfate heptahydrate was obtained in a pure state by recrystallizing a C.P. product three times from water. The salt was kept in a desiccator with a relative vapor tension of 70%.

Water: ordinary distilled water from the laboratory supply or in some instances conductivity water was used.

Hydrogen sulfide was prepared in a Kipp generator from commercial iron sulfide and passed through a wash bottle with sodium bicarbonate and another containing water.

Method of Precipitation: The method of treating the acid zinc-copper mixture with hydrogen sulfide is of primary importance. Previous workers have repeatedly noticed that it is very hard to get reproducible results in the amounts of zinc precipitated. This amount depends mainly upon the surface action of the copper sulfide and, therefore, fairly reproducible results can be expected only if the mixture is constantly shaken after the precipitation of the copper sulfide under a constant pressure of hydrogen sulfide. In the beginning of this work this important point was not realized and many experiments have been carried out according to procedure A (see below). With regard to the reproducibility of the results it may also be mentioned that in many

cases a distinct wall effect is noticed. In some instances (also in the absence of copper sulfide) the zinc sulfide separates as a thin, strongly adherent layer on the surface of the flask. Great attention was paid to a careful cleaning of the flasks with dichromate and sulfuric acid before they were used for the experiments. The wall effect seems to be more or less accidental. Special experiments by treating flasks with solutions of various types of ions in order to impart to the wall a positive or negative charge did not yield conclusive results. Even in flasks lined with paraffin, there is a noticeable wall effect.

Procedure A: The purified hydrogen sulfide gas was allowed to enter the space above the zinc-copper solution for about one minute. When all the air was displaced, the gas inlet tube (length 18 to 20 cm; inside diameter 5 to 6 mm.) was plunged into the solution and the gas allowed to bubble through the solution for a few minutes with shaking. The flasks after precipitation were tightly stoppered with rubber stoppers and allowed to stand or were mechanically shaken for various lengths of time. The concentration of hydrogen sulfide decreases on standing due to its diffusion from the flasks, its possible oxidation and the precipitation of zinc sulfide. In all cases sufficient experiments and blanks were run in order to justify the conclusions drawn from the results.

As has been discussed before the following *Procedure B* gives more reproducible results and is recommended for future work. After all of the air had been driven out of the system by a brisk stream of hydrogen sulfide (2-3 minutes) the inlet tube was pushed into the copper-zinc solution and precipitation was carried out for various periods of time with mechanical shaking. The flask was kept under constant hydrogen sulfide pressure in a mechanical shaker. The latter was driven by a motor which imparted a rotary motion in the horizontal plane to the solutions shaken. The eccentric displacement was sufficient to produce a decided movement without any splashing on to the stoppers.

Method of analysis: After filtration and washing (see below), the filtrates were boiled until all hydrogen sulfide was removed, cooled and titrated with potassium ferrocyanide using diphenylamine as an internal indicator. The details of this procedure will be described elsewhere (Ind. Eng. Chem., Anal. Ed. Jan. 1932).

In many cases the precipitated and washed copper sulfide was extracted with hot or cold hydrochloric acid (3 N to 4 N), most of acid evaporated and the residue titrated with ferrocyanide.

Results: In the first part of the work, the carrying down of zinc sulfide with copper sulfide was studied under various conditions (time, acidity, temperature). Since most of the results are in harmony with those of previous authors, it will suffice to summarize the most important conclusions which in part are new. The extensive experimental evidence is to be found in the thesis of E. A. Pearson.[25]

Zinc sulfide is not coprecipitated with copper sulfide but is "post-precipitated," the amount increasing with time of standing, decreasing with increas-

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[25] E. A. Pearson: Thesis, Minnesota 1931 p. 44-60, 97-108.

ing acidity of the solution (sulfuric acid or hydrochloric acid) and increasing with increasing temperature. Shaking favors the precipitation of zinc. The speed of passing through hydrogen sulfide during the precipitation of the copper sulfide also has a decided influence upon the amount of zinc post-precipitated, the latter increasing with rapid precipitation of the copper. Probably the total surface area of the copper sulfide increases with more rapid precipitation; this is another factor which has to be considered in the interpretation of the fact why it is so hard to obtain strictly reproducible results.

The effect of the presence of neutral salts ($NaCl$, KCl, NH_4Cl, $LiCl$, $CaCl_2$, $MgCl_2$) upon the precipitation of zinc sulfide generally is very small; the presence of sulfate (0.3 N) favors the precipitation but this is explained by a decrease of the hydrogen ion activity of the solution.

Effect of the Age of the Copper Sulfide

It has been mentioned already that more zinc is precipitated if the experiment is carried on at a high temperature than at room temperature. A few results given in Table I illustrate the large influence of the temperature.

TABLE I

Effect of the Age of the Copper Sulfide

25 cc. 0.05 molar copper sulfate, 25 cc. 0.05 molar zinc sulfate, 5 cc. 2.38 N sulfuric acid. Procedure B. Air was driven from system for seven minutes by hydrogen sulfide, then the gas was passed through the solution fairly rapidly with mechanical shaking for ten minutes. The precipitates were washed six times with warm water and then extracted with warm 2 N hydrochloric acid.

Temp. at beginning of precipitation	Temp. at end of precipitation	% Zn left in filtrate	% Zn extracted from precipitate	Remarks
23°	24°	92.3	7.1	Copper sulfide black appearance
23°	24°	91.0		,, ,, ,, ,,
24°	21°	92.5	7.1	,, ,, ,, ,,
24°	21°	93.7	6.4	,, ,, ,, ,,
100°	55°	4.8		Copper sulfide green slimy
100°	55°	5.1		appearance, hard to filter
100°	55°	5.0	91.0	
100°	55°	5.7	91.5	

An acid zinc solution alone precipitates more quickly at higher than at room temperature. The above experiments were repeated but instead of 25 cc. copper solution, 25 cc. of water were added. At the end of the ten minutes, the solution showed only a slight turbidity at room temperature, whereas 7.1 to 7.3% precipitated if the hydrogen sulfide were passed in at 100°. Comparing these figures with those in Table I, shows definitely that the copper

sulfide precipitated at higher temperature favors the post-precipitation of zinc much more than if precipitated at room temperature. The copper sulfide obtained at room temperature has a dark, black appearance and is easy to filter, whereas the sulfide formed at 100° is slimy; it has a greenish color and is hard to filter. That the latter favors the precipitation of zinc much more than copper sulfide formed at room temperature was definitely shown by the following experiments. (Compare with those in Table I). 25 cc. 0.05 molar copper sulfate, 5 cc. 2.38 N sulfuric acid. The mixture was heated to boiling, the air driven out with hydrogen sulfide for four minutes and again heated to 100°. The copper sulfide was precipitated in four minutes and the mixture cooled under hydrogen sulfide pressure to room temperature. Then 25 cc. 0.05 molar zinc sulfate were pipetted in and the mixture shaken for ten minutes under hydrogen sulfide (procedure B). As an average of four experiments, it was found that 13.5% ± 0.5% zinc was in the filtrate and 86% zinc in the precipitate. If the copper-zinc mixture was treated from the start with hydrogen sulfide at room temperature 91 to 93% of the zinc was found in the filtrate.

The last experiments and those described in Table I were repeated at various acidities and also under conditions in which the air had been removed by purified nitrogen before the treatment with hydrogen sulfide. Under all circumstances the same effect was noticed as described above.

If copper sulfide is precipitated at room temperature and allowed to age (under hydrogen sulfide) before the zinc solution is added its promoting effect upon the precipitation of zinc sulfide increases. Even after an hour standing the effect is quite pronounced, but it reaches a maximum after a day or more. The appearance of the copper sulfide changes from black to greenish; it becomes rather slimy and is hard to filter. It assumes the same appearance as the copper sulfide precipitated at 100°. If the latter is allowed to stand under hydrogen sulfide pressure its promoting effect upon the precipitation of zinc decreases and it becomes materially the same as that of the aged sulfide precipitated at room temperature (comp. Table II).

X-ray pictures (made by Professor N. H. Taylor) did not show a difference in crystal structure of the various copper sulfides, although the outer appearance is quite different. It was thought then that the cupric sulfide undergoes a decomposition on aging into cuprous sulfide and sulfur. A special investigation which will be described in a subsequent paper, however, showed that the amount of cuprous sulfide increases only very slightly on aging. Copper sulfide precipitated at room temperature contained only about 0.5% cuprous sulfide, after seven days aging 2%. Precipitates formed at 100° contained about 5% cuprous sulfide and after standing for nine days 7%. Moreover, it was shown by special experiments that the presence of cuprous sulfide in the copper sulfide does not affect its action upon the precipitation of zinc sulfide. Therefore, it seems that the temperature and aging effect are entirely functions of the surface, although we are led to the peculiar conclusion that copper sulfide precipitated at room temperature has a smaller surface than the same formed at 100° and that the extent of the surface in-

creases on standing. The surface of the sulfide precipitated at 100° decreases on standing and becomes about the same as that of the aged copper sulfide formed at room temperature in acid medium.

Table II. Effect of Aging of Copper Sulfide

25 cc. 0.05 molar copper sulfate and 5 cc. 2.88 N sulfuric acid. Air driven out with hydrogen sulfide, precipitated rapidly for two minutes with shaking. Flask tightly closed with rubber stopper and allowed to stand for some days. Then placed in series with the same mixture containing a fresh precipitate of copper sulfide prepared under exactly the same conditions. After saturating with hydrogen sulfide 25 cc. 0.05 molar zinc sulfide were added to each flask and treated fairly rapidly with hydrogen sulfide for ten minutes with shaking (Method B). After filtration the precipitates were washed four to six times with hot water (fresh precipitates) or 0.1 N ammonium sulfate (aged precipitates; to prevent passing through filter), and extracted with hot 4 N HCl.

Temp. of precipitation of copper sulfide	Age of copper sulfide	Appearance precipitate	% zinc in Filtrate	% zinc in Precipitate
24°	fresh	black	89.9	10.1
24°	1 day	green	36.5	65.7
24°	fresh	black	90.8	
24°	5 days	green	35.0	
25°	fresh	black	91.1	9.0
25°	6 days	green	40.4	59.2
25°	fresh	black	89.6	
25°	8 days	green	37.1	
90°	fresh	green	23.2	67.5
90°	5 days	green	35.5	64.
90°	fresh	green	25.0	75.0
90°	6 days	green	40.2	59.2

Incidentally, it may be mentioned that a slight oxidation of copper sulfide on aging could not be responsible for the effect observed. All experiments were repeated in such a way that the copper sulfide was allowed to age in flasks with a hole in the stopper. The results obtained were materially the same as those given in Table II.

The Effect of Adsorbed Hydrogen Sulfide

In the introduction it has been mentioned that part of the promoting action of copper sulfide upon the precipitation of zinc sulfide is attributed by the authors to hydrogen sulfide adsorbed on the surface of copper sulfide. Therefore, it could be expected that substances which displace hydrogen sulfide from the surface will inhibit the precipitation of zinc sulfide.

From colloidal chemical investigations, it is well known that metal sulfide sols owe their stability to adsorbed hydrogen sulfide. But also in

the flocculated state, these sulfides keep some hydrogen sulfide in the adsorbed state. This was proved for copper sulfide by a great number of experiments. Solutions of copper sulfate of known strength were treated under various conditions of acidity with standard solutions of sodium sulfide or hydrogen sulfide. Precautions were taken to limit the volatilization of the latter. An aliquot part of the supernatant liquid was pipetted out and added to an excess of an acid iodine solution which was titrated back with thiosulfate. Under various conditions, one mol copper sulfide adsorbed one to five mol per cent hydrogen sulfide, or alkali sulfide, this number increasing with the final concentration of sulfide or hydrogen sulfide in the solution and being only slightly dependent upon the acidity of the solution. In the experiments with copper sulfate and sodium sulfide, magnesium chloride had to be added in order to flocculate the copper sulfide.

Scheringa[14] claims that acid is strongly adsorbed by copper sulfide. The authors were not able to confirm this statement. Standard solutions of copper sulfate were treated with hydrogen sulfide, the mixture made up with water in a volumetric flask to the mark and in an aliquot part of the filtrate the acidity determined by titration with standard base after boiling off the hydrogen sulfide. No difference in titration figure was obtained between methyl orange or phenolphthalein as indicators. It was found that one millimol copper sulfide only adsorbs 0.003–0.014 millimoles sulfuric acid. Finally, it was shown that in shaking a fresh precipitate of copper sulfide with very dilute zinc solutions, none of the latter ion was adsorbed, which proves definitely that no solid solution is formed.

In studying the effect of substances which could displace hydrogen sulfide from the surface, it was expected that organic compounds containing a polar sulfur group would exert such an action. Actually it was shown that such substances are strongly adsorbed by copper sulfide.

In the interpretation of the effect of these polar substances upon the carrying down of zinc sulfide by copper sulfide certain difficulties arise which will be shortly discussed:

a. The organic substances used form complexes with cupric ions or reduce cupric copper to the cuprous state. Therefore, in studying their effect upon the after precipitation, the copper sulfide was first precipitated and thereafter the organic substance and the zinc added. This is not the most favorable experimental condition as the substance added has to displace the hydrogen sulfide which already is on the surface of the copper sulfide.

b. Zinc forms complexes with some of the substances used and, therefore, the latter may retard the precipitation of zinc sulfide alone in the absence of copper. For this reason in blank experiments in the absence of copper the influence of the added substance had to be studied on the precipitation of zinc alone. Some cases were found where the added substance retarded the precipitation of zinc sulfide alone, which may be attributed to complex formation or inhibition of the autocatalysis in the precipitation of the zinc (displacing hydrogen sulfide from the surface). Therefore, the theory was not conclusively supported if such a substance exerted an inhibiting effect upon

the precipitation of the zinc in presence of copper sulfide. Fortunately cases were met in which the added substance (cysteine, thiophenol) increased the speed of precipitation of zinc sulfide alone, whereas it inhibited its precipitation in the presence of copper sulfide.

Effect of Thiourea

The thiourea used was prepared from ammonium thiocyanate by the method of Reynolds[26] and purified by recrystallization. In later experiments an Eastman product was used which was found to be pure. All other compounds used (v.i.) were Eastman products with the exception of cysteine and glutathione. These latter compounds were kindly supplied by Dr. E. Kendall[27] of the Mayo Clinic and were of high degree of purity.

Table III. Adsorption of Thiourea by Copper Sulfide

25 cc. 0.25 molar copper sulfate, 0 to 15 cc. 4.07 N sulfuric acid. Copper sulfide precipitated moderately rapidly at room temperature. Allowed to stand with occasional shaking for two hours, after 25 cc. of a standard thiourea solution had been added. An aliquot part of the supernatant solution was pipetted out and after boiling off the hydrogen sulfide titrated with iodine. Blanks were run, in which the copper sulfate was replaced by an equal volume of water.

Molarity thiourea	cc. 4.07 N sulfuric acid added	Millimoles thiourea adsorbed by 6.25 millimoles CuS	% thiourea adsorbed from solution
0.05	0	0.137	10.8
0.05	5	0.165	13.1
0.05	10	0.109	8.7
0.01	0	0.101	40.5
0.01	1	0.104	41.5
0.01	5	0.100	40.0
0.01	10	0.086	34.2
0.005	0	0.033	27.7
0.005	5	0.047	39.2
0.005	10	0.047	39.2
0.005	15	0.045	36.9

Effect of Thiourea on the Precipitation of Zinc Sulfide

In the following table, it will be shown that thiourea retards the precipitation of zinc sulfide in the absence of copper sulfide. In the analysis the zinc was precipitated as carbonate and then titrated, in order to make the thiourea harmless.

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[26] Reynolds: J. Chem. Soc., **1903**, 7.

[27] The authors wish to express their thanks to Dr. E. Kendall for his kindness in supplying these valuable products.

Table IV. Effect of Thiourea on Precipitation of Zinc Sulfide

25 cc. 0.05 molar zinc sulfate, 25 cc. 0.05 molar thiourea (or 25 cc. water in blank), 5 cc. 2.21 N sulfuric acid and 25 cc. water. Air driven out for one minute then precipitated for four minutes under shaking. Tightly stoppered and mechanically shaken (Procedure A). Room temperature 28°.

Time of shaking	% zinc precipitated in absence of thiourea	% zinc precipitated in presence of thiourea
120 minutes	41.7	trace on wall
120 "	50.6	0.3 (on wall)
120 "	38.6	trace

The experiments were repeated but with 25 cc. 0.005 molar thiourea instead of 25 cc. 0.05 molar. Under these conditions an effect of the thiourea was hardly noticeable. Probably, thiourea forms a fairly stable complex with zinc ions.

Table V. Effect of Thiourea on Post-Precipitation of Zinc Sulfide in Presence of Copper Sulfide at Low Acidity

25 cc. 0.05 molar copper sulfate, 25 cc. 0.05 molar zinc sulfate and 5 cc. 4.07 N sulfuric acid. Precipitation at room temperature, then 25 cc. 0.05 molar thiourea added and 2.1 cc. 4.07 N sulfuric acid. In blanks, conditions were the same except 25 cc. of water were added after precipitation of copper sulfide, making the acidity in experiments and blanks the same (0.36 N). Flasks tightly stoppered and mechanically shaken for different periods of time. All precipitates washed four times with 0.36 N sulfuric acid saturated with hydrogen sulfide.

Temperature precipitation	Time of shaking	Presence thiourea		Blank	
		% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
22°	10 min.	98.4		90.0	11.0
32°	15 "	93.2	5.5	48.0	45.7
30°	20 "	77.8	13.0	43.7	50.3
30°	30 "	54.8	46.0	14.2	89.1
31°	30 "	51.5	42.7	11.1	85.0

The experiments were repeated at other acidities and varying acid concentrations. All showed that thiourea inhibits the precipitation of zinc sulfide in presence of copper sulfide. The results, however, do not prove anything definite about the influence of thiourea upon the mechanism of the reaction, since it exerts qualitatively the same influence upon the precipitation of zinc in the absence of copper sulfide.

Thiosemicarbazide behaves in the same way as thiourea. It is strongly adsorbed by copper sulfide and it retards the precipitation of zinc sulfide although not nearly as much as thiourea does and inhibits the precipitation in presence of copper sulfide.

Cysteine is strongly adsorbed by copper sulfide. No data are reported as no special precautions were taken to protect the cysteine hydrochloride solution from oxidation. It accelerates the speed of precipitation of zinc sulfide as is shown by the figures in Table VI.

Table VI. Effect of Cysteine on Speed of Precipitation of Zinc Sulfide

25 cc. 0.05 molar zinc sulfate, 25 cc. water and the indicated volume of sulfuric acid. Air was driven out with hydrogen sulfide for one minute and the gas passed through the solution for three minutes. Then 25 cc. 0.05 molar cysteine hydrochloride (or 25 cc. of water in the blank) were pipetted in and hydrogen sulfide passed in for one minute longer. Flask tightly stoppered and mechanically shaken. Precipitate washed four times with water.

Vol. Sulfuric acid added	Temp. during prec.	Time of shaking	Presence of cysteine % Zn in filtrate	Presence of cysteine % Zn in precipitate	Absence of cysteine % Zn in filtrate	Absence of cysteine % Zn in precipitate
5 cc. 2.21 N	39°	30 min.	34.3	65.2	68.2	31.8
,, ,,	33°	60 min.	43.8	56.2	68.8	31.0
5 cc. 3.91 N	32°	60 min.	76.8	23.2	98.0	2.0
,, ,,	32°	125 min.	69.2	30.8	94.1	5.7
,, ,,	26°	180 min.	86.8	13.2	97.1	2.9
					94.5	5.7

From the results in Table VII it is evident that cysteine inhibits the precipitation of zinc sulfide in the presence of copper sulfide although it accelerates the precipitation of zinc sulfide alone. This behavior is in harmony with our theory based upon the displacement of adsorbed hydrogen sulfide by cysteine.

Table VII. Effect of Cysteine on Precipitation of Zinc in Presence of Copper Sulfide

25 cc. 0.05 molar copper sulfate, 25 cc. 0.05 molar zinc sulfate and 5 cc. 2.21 N sulfuric acid. Hydrogen sulfide passed through for three minutes and then 25 cc. 0.05 molar cysteine hydrochloride (or in blank 25 cc. water) added; the gas passed through for one to two minutes longer. The cysteine is made harmless in the titration of zinc by oxidation with an excess of bromine water, the latter being removed by boiling.

Temp. during precipitation	Time of shaking	Presence of cysteine % Zn in filtrate	Presence of cysteine % Zn in Precipitate	Blank % Zn in filtrate	Blank % Zn in precipitate
25°	15 min.	88.4	11.5	83.4	18.0
25°	30 ,,	80.0	20.0	52.8	48.0
39°	20 ,,	13.0	82.2	5.2	94.0

With 5 cc. 3.91 N sulfuric acid instead of 5 cc. 2.21 N

31°	10 min.	96.8	2.0	85.7	11.4
31°	20 ,,	93.0	6.1	71.3	28.1

Glutathione retards the precipitation of zinc sulfide alone and behaves similarly to thiourea and thiosemicarbazide. It also inhibits the aging of copper sulfide at room temperature.

Thiophenol on the other hand, accelerates the precipitation of zinc sulfide alone, but has an inhibiting effect in the presence of copper sulfide. For example in the precipitation of zinc sulfate alone (conditions somewhat similar to those in Tables IV and VI), 64% was precipitated after one hour in the presence of thiophenol and only 7.6% in the blank.

The results in Table VIII show its inhibiting effect in the presence of copper sulfide.

Table VIII.   Effect of Thiophenol on Precipitation of Zinc in Presence of Copper Sulfide (30°)

Time of shaking	Presence of thiophenol		Blank	
	% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
11 min.	88.2	11.0	80.3	17
20 "	85.8	12.0	73.6	22
30 "	67.8	30.9	61.0	35
80 "	45.3	53.0	32.5	63

Thiobarbituric acid inhibits the precipitation of zinc alone although its effect is very small. However, it has a pronounced inhibiting effect upon the speed of precipitation of zinc in the presence of copper sulfide.

Summarizing, it appears that cysteine, thiophenol and thiobarbituric acid, which are strongly adsorbed by copper sulfide, accelerate the precipitation of zinc sulfide alone, whereas they inhibit the speed in the presence of copper sulfide. This behavior is a good support for our theory that adsorbed hydrogen sulfide on the surface of copper sulfide is partly responsible for its promoting effect upon the precipitation of zinc sulfide, although it is not quite conclusive as the polar substances may change the surface of the copper sulfide in a more radical way.

Influence of Various Substances upon the Speed of Precipitation of Zinc Sulfide

It has been mentioned in the introduction that the promoting effect of copper sulfide on the precipitation of zinc sulfide is not specific for this substance, but that all finely divided substances will exert more or less the same influence. Experimental evidence for this conclusion is given in the following pages. In order to show the promoting effect of the substances used it was necessary to work at a lower acidity than was done in the experiments with copper sulfide.

With regard to the "wall effect" it was of interest to study the influence of powdered Pyrex glass, silica gel and the difference in behavior between a paraffined wall and a flask etched with hydrogen fluoride.

Table IX. Influence of Powdered Pyrex Glass on Precipitation of Zinc Sulfide

25 cc. 0.05 molar zinc sulfate and the indicated volume of sulfuric acid, air driven out for two minutes then treated with hydrogen sulfide (procedure B). Temperature 22°.

cc. sulfuric acid	Time of shaking	% Zn in filtrate without pyrex powder	Pyrex powder added	% Zn in filtrate in presence of pyrex powder
1 cc. 2.88 N	10 min.	57.2	1 g.	27.9
,, ,,	,,	58.3	1 g.	37.8
3 cc. 2.88 N	32 ,,	98.9	3 g.	86.2
5 cc. 2.88 N	60 ,,	99.5	5 g.	99.7

In the experiments with silica gel a product was used with a high adsorbent power which had been purified by electrodialysis. The adsorption of mineral acid by this silica gel was negligibly small, hence, the promoting effect upon the precipitation of zinc sulfide is not due to a decrease of the acidity of the solution. The effect of silica gel is given in Table X.

Table X. Influence of Silica Gel on Precipitation of Zinc Sulfide

25 cc. 0.05 molar zinc sulfate, 50 cc. water and the indicated amount of sulfuric acid. Air driven out for one minute then hydrogen sulfide passed through solution rapidly for three minutes. Flask tightly stoppered and mechanically shaken. One gram of silica gel was used. Temperature 28°–29°.

cc. sulfuric acid added	Time of shaking	Absence of silica gel		Presence 1 g. silica gel	
		% Zinc in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
5 cc. 2.21 N	15 min.	93.9	6.1	88.5	11.0
,, ,,	20 ,,	98.2	1.8	75.5	22.8
,, ,,	30 ,,	89.0	11.0	63.1	33.3
5 cc. 3.91 N	30 ,,	100.0	0.0	99.4	0.6

It has been mentioned before that in many cases a definite "wall effect" was noticed in the precipitation of zinc sulfide. Since finely divided glass favors the precipitation of zinc, it may be expected that quantitatively this wall effect will depend upon the smoothness of the glass. A coarse surface will favor the precipitation more than an etched surface. A mixture of 50 cc. 0.025 molar zinc sulfate and 2 cc. 2.88 N sulfuric acid was treated in paraffined and etched (with HF) flasks respectively with hydrogen sulfide (Procedure B; mechanical shaking). In all cases more zinc was precipitated in the etched than in the paraffined flask. However, it was found that some of the zinc also precipitated on the paraffined wall. Some figures show that the effect of etching is relatively small: % zinc precipitated: 89.5% (paraffined); 86.9% (etched); 87.7% (paraffined;) 83.3% (etched); 90.0% (paraffined); 82.6% (etched); 92.0% (paraffined); 90% (etched).

Effect of Barium Sulfate

It was found that barium sulfate powder promotes the precipitation of zinc sulfide.

Table XI. Effect of Barium Sulfate

25 cc. 0.05 molar zinc sulfate and 3 cc. 2.88 N sulfuric acid. Procedure B. Temperature 24°. 3 g. barium sulfate C.P. added.

Time of shaking	Absence of barium sulfate		Presence of barium sulfate	
	% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
31 min.	95.8	4.2	86.5	13.2
145 ″	97.4	2.4	38.8	61.1

Effect of Sulfur

A large number of experiments were carried out to study the effect of colloidal sulfur obtained by reaction of iodine with hydrogen sulfide or according to Oden's method. In most cases the sol flocculated very rapidly in the electrolyte solution and, therefore, a relatively small surface was exposed to the liquid. In all cases, however, it was found that sulfur promotes the precipitation of zinc sulfide. The next table shows that sublimed sulfur also exerts a distinct effect.

Table XII. Effect of Resublimed Sulfur

50 cc. 0.025 molar zinc sulfate and 2 cc. 2.88 N sulfuric acid. One g. of sulfur added. Method B. Temperature 21°.

Time of shaking	Absence of sulfur % Zn in filtrate	Presence of 1 g. of sulfur % Zn in filtrate
10 min.	87.5	51.3
15 min.	80.0	42.4

Effect of Charcoal

Table XIII shows the promoting effect of charcoal (Merck product, ash-free, highly activated).

Table XIII. Effect of Activated Ash-Free Charcoal

25 cc. 0.05 molar zinc sulfate, 50 cc. of water and 5 cc. 2.21 N sulfuric acid. 300 mg. charcoal. After precipitation flask tightly stoppered and mechanically shaken. Temperature 28°.

Time of shaking	Absence of charcoal		Presence of charcoal	
	% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
10 min.	95.0	5.0	85.4	14.5
15 ″	94.6	5.4	78.4	20.3
20 ″	93.5	6.5	68.9	31.1
30 ″	88.5	11.5	70.0	29.5

Ignited Aluminum Oxide

Ignited aluminum oxide promotes the precipitation of zinc sulfide very strongly. Part of this, however, is due to a strong adsorption of sulfuric acid on the oxide by which the acidity of the solution is greatly decreased.

In special experiments, the amount of acid adsorbed after a certain period of time was determined and correspondingly more acid was added to the zinc solution to make up for the amount disappearing by the adsorption. A description of all experiments would require too much space, therefore, the statement will do that ignited aluminum oxide promotes the precipitation of zinc sulfide very strongly.

Effect of Talc

The talc used (U.S.P.) was purified by digesting with boiling strong hydrochloric acid and washing free from acid. Table XIV shows the distinct promoting effect of talc.

Table XIV.   Effect of Talc

50 cc. 0.025 molar zinc sulfate and indicated amount of sulfuric acid. Precipitated fairly rapidly with mechanical shaking. Procedure B. Temperature 24°.

cc. sulfuric acid added	Time of shaking	grams talc added	Absence of talc		Presence of talc	
			% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
2 cc. 2.88 N	10 min.	1 g.	90.7	9.0	71.6	28.0
,, ,,	10 ,,	2 g.	92.0	8.0	42.7	57.3
5 cc. 2.88 N	30 ,,	2 g.	100.0	0.0	98.8	1.0

Effect of Filter Paper

Ash-free filter paper was finely divided and vigorously shaken with water. The suspension was added to the zinc sulfate solution.

Table XV.   Effect of Filter Paper

25 cc. 0.05 molar zinc sulfate, 25 cc. filter paper suspension (or 25 cc. water in blank) and indicated amount of zinc. Method B. Time of standing 30 minutes. Temperature 23°–25°.

cc. sulfuric acid added	Speed of passing through hydrogen sulfide	Absence filter paper		Presence filter paper	
		% Zn in filtrate	% Zn in precipitate	% Zn in filtrate	% Zn in precipitate
5 cc. 2.88 N	Slow	97.6		97.5	
2 ,, ,,	Mod. rapidly	75.9	24.1	67.6	32.4
2 ,, ,,	,, ,,	85.7	14.3	68.9	31.0

It is seen that even filter paper promotes the precipitation of zinc sulfide slightly.

Summary

1.   The "carrying down" of zinc sulfide by copper sulfide cannot be attributed to a coprecipitation (occlusion), a mixed crystal formation, or distribution of the zinc between solution and the solid. The zinc sulfide precipitates after the copper sulfide has been quantitatively formed. The

copper sulfide promotes the precipitation of zinc sulfide by virtue of its finely divided state and the presence of an adsorbed layer of hydrogen sulfide on its surface.

2. Copper sulfide precipitated at room temperature has a smaller promoting effect than that formed at boiling temperature. On standing the copper sulfide formed at room temperature shows an increased promoting effect, that precipitated at high temperature a decreasing effect. After aging for a few days at a certain acidity both precipitates have the same effect. On standing the precipitate formed in the cold assumes the same appearance as that obtained at high temperature.

3. Cysteine and thiophenol accelerate the precipitation of zinc sulfide alone, but inhibit its precipitation in the presence of copper sulfide. This was expected on the basis of the adsorption theory.

4. Finely divided substances, such as glass powder, silica gel, barium sulfate, charcoal, sulfur, talcum, aluminum oxide and filter paper promote the precipitation of zinc sulfide, showing the general character of the surface effect upon the speed of formation of a precipitate from a supersaturated solution.

School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota.
1931.

PHOTO-SYNTHESIS IN TROPICAL SUNLIGHT. PART III
Synthesis of Formaldehyde

BY ATMA RAM RAJVANSI AND N. R. DHAR

In two previous communications from these laboratories, Gopala Rao and Dhar have reported their work on the photo-synthesis of formaldehyde and carbohydrates in tropical sunlight. Further work has been done by us in this line and will form the subject matter of Parts III and IV.

Reduction of Carbon Dioxide to Formaldehyde in the Presence of Photocatalysts and Sunlight

Carbon dioxide prepared from marble and dilute hydrochloric acid and purified by passage through two or three wash-bottles containing distilled water was passed through a two-way tube into two glass beakers, one containing conductivity water and the other containing conductivity water to which the photosensitizer has been added. Both the beakers were covered with clock glasses and exposed to the bright sun. The object of keeping a blank was to avoid the question of formaldehyde formation being attributed to impurities. After sufficient exposure, the contents of both the beakers were tested for formaldehyde. Other details of the experimental procedure were the same as those described in Part I of this series.

In all the previous work on the reduction of carbon dioxide to formaldehyde, no attempt has been made to estimate quantitatively the amount of formaldehyde. An attempt in this direction has now been made. We do not claim, however, that the results are absolutely quantitative. The yield of formaldehyde, in each case starting with a definite and equal volume of solution and allowing it to be exposed for the same amount of time and also distilling to the same extent, has been determined by comparing the tint of the colour produced by using standard solutions of formaldehyde already prepared. Schryver's reagent was utilized throughout for testing formaldehyde.

The results are summarised in Table I:

TABLE I

Experiments	Time of exposure	Results
1. CO_2 passed in conductivity water.	4 hrs.	very small amounts of formaldehyde detected.
2. CO_2 passed in nickel sulphate.	do.	formaldehyde detected, no sugar.
3. CO_2 passed in nickel carbonate.	do.	formaldehyde detected, but no sugar.

TABLE I (Continued)

Experiments	Time of exposure	Results
4. CO_2 passed in chromium oxide.	do.	formaldehyde detected, no sugar.
5. CO_2 passed in chromium sulphate.	do.	formaldehyde detected, no sugar.
6. CO_2 passed in copper carbonate.	do.	formaldehyde detected, no sugar.
7. CO_2 passed in copper acetate.	do.	formaldehyde detected, but no sugar.
8. CO_2 passed in copper sulphate.	do.	formaldehyde detected, no sugar.
9. CO_2 passed in copper chloride.	do.	formaldehyde detected, no sugar.
10. CO_2 passed in ferric chloride.	do.	little formaldehyde detected, no sugar.
11. CO_2 passed in ferrous sulphate.	do.	little formaldehyde detected.
12. CO_2 passed in ceric ammonium nitrate.	do.	little formaldehyde detected.
*13. CO_2 passed in cobalt carbonate.	do.	formaldehyde detected in greater amounts than any previous one, no sugar.
14. CO_2 passed in colloidal V_2O_5	do.	not much formaldehyde.
15. CO_2 passed in vanadic acid	do.	small amounts of formaldehyde.
*16. CO_2 passed in $MnCl_2$	do.	greatest amounts of formalde-hyde detected so far, no sugar.
17. CO_2 passed in phospho-molybdic acid.	4 hrs.	no formaldehyde, no sugar.
18. CO_2 passed in molybdic acid	do.	no formaldehyde, no sugar and no change in colour of the solution.
19. CO_2 passed in ceric oxide.	do.	no formaldehyde, no sugar.
20. CO_2 in sodium phospho-molybdate.	do.	no formaldehyde, no sugar.
21. CO_2 passed in praseodymium nitrate.	do.	small amounts of formalde-hyde detected, no sugar.
22. CO_2 passed in yittrium nitrate.	do.	no formaldehyde, no sugar.
23. CO_2 passed in ceric sulphate.	do.	formaldehyde in small quantities, no sugar.
24. CO_2 passed in colloidal ferric hydroxide.	do.	small quantities of formal-dehyde, no sugar.

TABLE I (Continued)

Experiments	Time of exposure	Results
25. CO_2 passed in colloidal chromium hydroxide.	do.	very small amounts of formaldehyde.
26. CO_2 passed in uranium nitrate.	do.	small amounts of formaldehyde.

Organic Photocatalysts

27. CO_2 passed in chlorophyll suspension.	do.	formaldehyde detected in greater amounts than when chlorophyll itself was exposed and distilled, no sugar.
28. CO_2 passed in methylene blue	do.	little of formaldehyde detected, no sugar.
29. CO_2 passed in malachite green.	do.	small amounts of formaldehyde, no sugar.
30. CO_2 passed in methyl orange.	do.	formaldehyde detected, no sugar.
31. CO_2 passed in safranine.	do.	no formaldehyde detected, no sugar.
32. CO_2 passed in rhodamin.	do.	no formaldehyde, no sugar.
33. CO_2 passed in cartharamin.	do.	no formaldehyde, no sugar.
34. CO_2 passed in bordeaux red.	do.	no formaldehyde, no sugar.
35. CO_2 passed in neutral red.	do.	very little of formaldehyde, no sugar.
36. CO_2 passed in fluorescein.	do.	no formaldehyde, no sugar, the dye decolourised.
37. CO_2 passed in ferric chloride.	12 hrs.	small amounts of formaldehyde and very little of sugar.
38. CO_2 passed in cobalt carbonate.	do.	formaldehyde detected in appreciable amounts, no sugar.

N.B. In all the cases studied the fluorescent dyes were decolourised when exposed to the sunlight.

Table II contains the results of the *semi-quantitative* experiments carried out following the process mentioned already, the time of exposure being 4 hours in each case.

TABLE II

Experiments	Percentage of formaldehyde in visible light	Percentage of formaldehyde in ultraviolet light
1. CO$_2$ passed in conductivity water.	not much	0.00002% by vol.
2. CO$_2$ passed in MnCl$_2$ solution.	0.0008% by vol.	0.00087% by vol.
3. CO$_2$ passed in nickel carbonate.	0.00008% by vol.	0.000083% by vol.
4. CO$_2$ passed in copper sulphate.	0.000081% by vol.	0.000083% by vol.
5. CO$_2$ passed in cobalt carbonate.	0.0006% by vol.	0.00062% by vol.
6. CO$_2$ passed in copper acetate.	0.00004% by vol.	0.000043% by vol.
7. CO$_2$ passed in chromium oxide.	0.00006% by vol.	0.000061% by vol.
8. CO$_2$ passed in malachite green.	0.00006% by vol.	0.000066% by vol.
9. CO$_2$ passed in cobalt chloride.	0.00004% by vol.	0.000042% by vol.
10. CO$_2$ passed in nickel sulphate.	0.00004% by vol.	0.00004% by vol.
11. CO$_2$ passed in uranium nitrate	0.00005% by vol.	0.000053% by vol.

In many other cases in which positive results for formaldehyde have been obtained, the amount of formaldehyde was generally between 0.000042 to 0.00005% by volume. It will be clear from the above results, that ultraviolet light increases the yield of formaldehyde.

The Photosynthesis of Formaldehyde and Carbohydrates from Alkali Bicarbonates and Pure CO$_2$

That solutions of bicarbonates of alkali metals when exposed to sunlight decompose into carbon dioxide and sodium carbonate is a well known fact. That this evolved carbon dioxide may be utilised to effect a synthesis of formaldehyde and carbohydrates. Dilute solutions of NaHCO$_3$ usually 3% were prepared in conductivity water. Merck's or Kahlbaum's samples of NaHCO$_3$ were used. The solutions were exposed in glass bulbs blown at the ends of common soft glass tubes having a diameter of one cm. and 1 or 1½ ft. long and a capacity of nearly 200–250 c.c. The bulbs were cleaned with hot chromic acid and also with boiling caustic soda to remove any grease or dust. After carefully cleaning and washing several times with conductivity water they were dried well. The solutions to be exposed with or without photocatalysts were filled up in the bulbs and sealed at the ends with a

little space above the solutions. The bulbs while exposed to sunlight were kept in glass jars filled with water at a constant temperature for a period of 40 to 60 hours. As has already been pointed out the bulbs were made of soft glass and in a tropical country like India sunlight on sunny days consists of light of wave-lengths up to 3000 or 2900 Å; the portion of the ultraviolet light which is present in the sunlight is thus mostly cut off in these experiments as glass cuts off most of the ultraviolet rays below 3400 Å. Thus the above experiments have been performed in the practical absence of ultraviolet light.

After sufficient exposure, the ends of the bulbs were broken and the contents filtered, if an insoluble catalyst was used. The filtrate was distilled

Table III

Experiments	Time of exposure	Results
1. CO_2 and conductivity water sealed in a bulb.	80 hrs.	very small quantities of formaldehyde but no sugar.
2. CO_2 with chromium oxide in a sealed bulb.	60 hrs.	formaldehyde detected, no sugar.
3. CO_2 with nickel sulphate in a sealed bulb.	do.	small quantity of formaldehyde, but no sugar.
4. CO_2 with nickel carbonate in a sealed bulb.	do.	some formaldehyde, but no sugar.
5. CO_2 with cobalt carbonate in a sealed bulb.	do.	some formaldehyde, but no sugar.
6. 3% sodium bi-carbonate in a sealed bulb.	do.	small quantities of formaldehyde, but no sugar.
7. 3% sodium bicarbonate solution with nickel carbonate in a sealed bulb.	70 hrs.	small quantities of formaldehyde, but not sufficient sugar to reduce Benedict's solution, but there is some changing with conc. sulphuric acid.
8. 3% sodium bicarbonate and chromium oxide in a sealed bulb.	80 hrs.	very small quantities of formaldehyde, but no sugar.
9. 3% sodium bicarbonate and copper carbonate in a sealed bulb.	60 hrs.	small quantities of formaldehyde, but no sugar.
10. 3% sodium bicarbonate and copper acetate in a sealed bulb.	do.	appreciable quantity of formaldehyde, but no sugar to reduce Benedict's solution but there is charring.
11. 3% sodium bicarbonate with colloidal ferric hydroxide.	do.	very little formaldehyde, no sugar, but the sol coagulates.

and several distillates collected; the distillates so collected were tested for formaldehyde as already described. The portion of the filtrate which remained in the distilling flask was tested for sugars and carbohydrates. The filtrate was usually filtered again and evaporated to dryness and extracted with absolute alcohol. All the tests used in this investigation were those described by Plimmer in his "Practical Organic and Biochemistry." For testing sugars Benedict's solution was used as formaldehyde also reduces Fehling's solutions. If the Benedict's solution was not reduced by the solution to be tested, the solution was hydrolysed by HCl, the excess of HCl was neutralised and the hydrolysed solution again tested with Benedict's solution. In this way it was possible to test the disaccharides which might have been synthesised during the polymerisation process. Table III shows the results obtained in these experiments.

In all these cases bulbs with the same amount of the solution and photocatalysts were always kept in the dark. The entire failure to detect any formaldehyde or carbohydrates in these bulbs clearly points out the importance of light and establishes beyond doubt that the conversion of carbon dioxide into formaldehyde is only possible in presence of sunlight. The above experiments were carried out in visible light as in every case glass bulbs were used. However in order to study the effect of ultraviolet light two pyrex beakers containing the same amount of sodium bicarbonate solution were exposed to sunlight, one of them being covered with a clock glass and the other left open. After 5 or 6 hours' exposure both of them were distilled to the same extent and the distillates tested for formaldehyde. The beaker which was left uncovered gave a greater yield of formaldehyde than the one which was

TABLE IV

Experiments	Time of exposure	Amount of formaldehyde when the solution was half distilled
1. 25 c.c. of 3% $NaHCO_3$ in a *pyrex* glass beaker *covered* with a clock glass.	6 hrs.	0.0032% formaldehyde, no sugar.
2. 25 c.c. of $NaHCO_3$ solution in a *pyrex* glass beaker *uncovered*.	do.	0.004% formaldehyde, no sugar.
3. 25 c.c. of $NaHCO_3$ solution in a *Jena* glass beaker *covered* with a watch glass.	7 hrs.	0.0035% formaldehyde, no sugar.
4. 25 c.c. of 3% $NaHCO_3$ in a *quartz* beaker *covered* with a quartz cover.	do.	0.0045% formaldehyde, no sugar.

Similar solutions were kept in the dark and distilled; the distillate tested for formaldehyde gave negative results.

covered. This was due to the fact that in the uncovered beaker most of the ultraviolet rays of sunlight were utilised while they were practically cut off in the other case. Not content with this, as it might be argued that some formaldehyde might have been formed in the open beaker due to the dust of the atmosphere, we used a quartz beaker covered with a quartz cover. It was very clearly established from the results of these latter experiments that ultraviolet light certainly plays a prominent part in photosynthesis. Table IV contains the results obtained:

Photosynthesis of Formaldehyde from Nascent Carbon Dioxide

The synthesis of formaldehyde from $NaHCO_3$ solution without the addition of a photocatalyst clearly pointed out that there is some difference in using ordinary carbon dioxide and nascent carbon dioxide. It appears that the nascent carbon dioxide in the case of $NaHCO_3$ solution, was responsible for the formation of formaldehyde when $NaHCO_3$ solution was exposed to sunlight and an attempt therefore was made to effect the synthesis of formaldehyde and carbohydrates from nascent carbon dioxide. An ordinary flask was taken in which some Merck's barium carbonate was placed under conductivity water. A burette of 50 c.c. capacity was filled with pure $N/20$ HCl. A double bored cork was fitted in the flask and in one of the holes the burette was attached to the flask. The flow of HCl was so arranged that 50 c.c. of it from the burette flowed in the flask in four hours. The whole apparatus was kept in bright sunlight. What happened was this, that as soon as a dilute HCl drop reached the flask it reacted with $BaCO_3$ and CO_2 in the nascent state was evolved. This nascent CO_2 absorbing sun light reacted with the water present in the flask with the production of formaldehyde. In this way it was possible to use nascent CO_2 for photosynthetic purposes. A similar arrangement was also exposed side by side as a blank experiment. In this case no HCl was allowed to flow from the burette, but pure conductivity water. The volume of conductivity water originally taken in both the flasks was the same. At the end of four hours both the flasks contained the same amount of water. The amount of $BaCO_3$ left unacted upon was filtered and the filtrate was distilled in several fractions. The distillates from both the flasks were tested for formaldehyde. The remaining portion of the undistilled liquid in the distilling flask was tested for sugars as already described. Another set of experiments was performed using in the apparatus only pure water and no $BaCO_3$, but HCl was run down from the burette. Another blank was exposed containing only $BaCl_2$ in the reaction flask. All these sets of experiments were repeated with $CaCO_3$, $SrCO_3$, Na_2CO_3. The failure to detect formaldehyde in the blank experiments and the experiments repeated several times established the accuracy of the experiments and conclusions. Similar flasks were put in the dark, no formaldehyde was detected in any case. A comparison using a quartz flask was made in order to see the effect of ultraviolet light.

Table V contains the results obtained with these experiments:

TABLE V

Experiments	Time of exposure	Results
1. $BaCO_3$ in the flask and HCl run from the top in ordinary *glass flask*.	4 hrs.	0.0002% of formaldehyde, no sugar.
2. $CaCO_3$ in the flask and HCl run from the top.	do.	0.00018% formaldehyde, no sugar.
3. $SrCO_3$ in the flask and HCl run from the top.	do.	0.00018% formaldehyde, no sugar.
4. Na_2CO_3 in the flask and HCl run from the top.	do.	0.00018% formaldehyde, no sugar.
5. $BaCO_3$ with water in the flask and *only* water run from the top (blank).	4 hrs.	No formaldehyde, no sugar.
6. Water in the flask and HCl run from the top.	do.	No formaldehyde, no sugar.
7. $BaCl_2$ in the flask and HCl run from the top.	do.	No formaldehyde, no sugar.
8. $BaCO_3$ in *quartz flask* and HCl run from the top.	do.	0.00025% formaldehyde, no sugar.

Summary

1.   Formaldehyde has been obtained from carbon dioxide and water in the presence of the following sensitizers and sunlight: (1) chromium oxide, (2) cobalt carbonate, (3) nickel carbonate, (4) manganous chloride, (5) copper carbonate, (6) nickel sulphate, etc.   Of these manganous chloride and cobalt carbonate appear to be the best.   Some of the dyestuffs like methylene blue and malachite green are also good photosensitisers.   It is interesting that many fluorescent dyestuffs do not bring about the synthesis of formaldehyde from carbon dioxide and water.

2.   Formaldehyde has also been obtained by exposing solutions of the alkali bicarbonates with several photosensitizers.

3.   With nascent carbon dioxide obtained by the interaction of carbonates and hydrochloric acid no coloured photo-sensitizer appears to be necessary for the formation of formaldehyde.

In all these cases the yield of formaldehyde is about fifty to thirty times the sensitiveness of the colour test.   In view of this fact and the elaborate and careful blank experiments always performed, there is no doubt that formaldehyde is actually formed from carbon dioxide and water in presence of sunlight.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
June 4, 1931.

PHOTO-SYNTHESIS IN TROPICAL SUNLIGHT. PART IV

Synthesis of Sugars and Complex Nitrogenous Substances

BY ATMA RAM RAJVANSHI AND N. R. DHAR

In a previous paper we have recorded our results on the photosynthesis of formaldehyde. In this paper we will deal with (1) polymerisation of formaldehyde to reducing sugars, (2) synthesis of complex nitrogenous compounds and (3) discussion of results recorded in both the papers.

Polymerisation of Formaldehyde to Reducing Sugars

It was Butlerow[1] who for the first time showed that formaldehyde is polymerised to reducing sugars when heated with dilute alkalies. Nef[2] has shown that this mixture of reducing sugars, so obtained, contains nearly 24 members of the carbohydrate family. The condensation of formaldehyde to reducing sugars by means of sunlight has been recently studied by Baly and co-workers[3] who have reported the formation of sugars from dilute solutions of formaldehyde in ultraviolet light. Dhar and Sanyal,[4] Gopala Rao and Dhar have reported the formation of sugars from formaldehyde solutions exposed to sunlight in presence of ferric chloride, chlorophyll and zinc oxide.

Aqueous solutions of formaldehyde (Merck's formalin 40%) usually 3% were prepared using pure water, and exposed in pyrex glass beakers and sealed bulbs for a period extending over 60 to 100 hours and some times even 125 hours. These solutions were also exposed in big sealed bulbs having a capacity of 200 to 250 cc. using different photocatalysts. Similar solutions were kept in bulbs and beakers in the dark. The solutions exposed and unexposed were examined simultaneously and always Benedict's solution was used to test sugars as Fehling's solution is also reduced by formaldehyde. The procedure of removing the sugars was the same as described already. In Table I are the results obtained with these experiments.

Temperature Coefficient of Sugar Formation

A study of the temperature coefficient of sugar formation from HCHO was undertaken with a view to the elucidation of the process of polymerisation of HCHO to sugars. The experimental procedure adopted was as follows:

Two big bulbs of ordinary glass whose capacity was one litre were well cleaned with hot chromic acid and subsequently with hot caustic soda solution in order to remove any impurity present. Two litres of 3% formaldehyde

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[1] Ann., 111, 242 (1859); Compt. rend., 53, 145 (1861).

[2] Ann., 403, 355 (1914).

[3] J. Chem. Soc., 121, 1078 (1922); 123, 165 (1923); Proc. Roy. Soc., 116A, 197, 212 219 (1927); 122, 393 (1929).

[4] J. Phys. Chem., 29, 926 (1925).

TABLE I

Experiments	Time of exposure	Results
1. 3% HCHO	100 hrs.	no sugar detected.
2. 3% HCHO with ferric chloride in a beaker	40 hrs.	sugar detected.
3. 3% HCHO with chlorophyll	40 hrs.	sugar detected, but less than the previous case.
4. 3% HCHO with ZnO	70 hrs.	very small quantity of sugar.
5. 3% HCHO with methyl orange	50 hrs.	very small quantity of sugar.
6. 3% of HCHO with methylene blue	70 hrs.	very little of sugar.
7. 3% HCHO with nickel carbonate	do.	little reducing sugar.
8. 3% HCHO with FeSO₄	90 hrs.	very little reducing sugar.
9. 3% HCHO with MgO	100 hrs.	no sugar.
10. 3% HCHO with BaCO₃	do.	do.
11. 3% HCHO with CaCO₃	do.	do.
12. 3% HCHO with SrCO₃	do.	do.
13. do. CuCO₃	do.	do.
14. do. CuSO₄	do.	do..
15. do. uranium nitrate	80 hrs.	do.
16. do. safranine	100 hrs.	do.
17. do. cartharamin	do.	do.
18. do. rhodamin	do.	do.
19. do. cobalt carbonate	75 hrs.	do.
20. do. SnO	80 hrs.	do.
21. do. chromium sulphate	90 hrs.	do.
22. do. nickel sulphate	do.	do.
23. do. Ca(OH)₂	70 hrs.	do.
24. do. erythrosin	do.	do.
25. do. phosphomolybdic acid	do.	do.
26. do. praseodymium nitrate	do.	do.
27. do. yttrium nitrate	do.	do.
28. do. ceric oxide	do.	do.
29. do. ferric chloride in a sealed tube	50 hrs.	appreciable amounts of sugar.
30. 3% HCHO with ferric chloride and little ferrous sulphate	50 hrs.	less than in the previous case.
31. do. chlorophyll in a sealed tube	do.	more sugar than in the beaker.
32. do. with ferric hydroxide sol	do.	no reducing sugar.

solution were prepared and an excess of ferric chloride was added, because some of the ferric chloride is reduced to ferrous chloride by the action of formaldehyde. 800 cc. of this solution were filled in each bulb and the bulb sealed at the end. The bulbs were put in big glass jars used as a thermostat and exposed to the bright sunlight. The temperature of the two jars was kept constant at 30° and 40° C respectively. After an exposure of 45 hours, the two bulbs were removed and their ends broken. 750 cc. of the contents were taken from one bulb and the ferrous salt produced during the exposure (the ferrous salt also reduces Benedict's solution) and some ferric chloride left were first removed by precipitating them with ammonia as hydroxides. After the whole of ferrous and ferric chloride were removed, the remaining solution was evaporated on a water bath to dryness. The dried mass was extracted with pure methyl alcohol. The extract was then evaporated on a water bath and dissolved in water. A similar process was adopted with the contents of the other bulb. A small quantity of the solution, so obtained, was tested for HCHO and in both cases negative results were obtained. 40 cc. of a standard Fehling's solution were heated on a water bath for half an hour and the first solution added to it. A marked reduction of the Fehling's solution was noticed. After a complete reaction the cuprous oxide was well washed, dried, ignited, and weighed as cupric oxide. Similarly the solution obtained from the other bulb was treated with Fehling's solution and the cupric oxide weighed.

The following are the results obtained:—

1. at 30° C. Wt. of CuO = 0.061 gm.
2. at 40° C. Wt. of CuO = 0.077 gm.

Temperature coefficient (0.077/0.061) = 1.2 nearly

1. the wt. of sugar calculated as glucose at 30° C. = 0.1355 grm.
2. the wt. of sugar calculated as glucose at 40° C. = 0.16 grm.

We have discussed later on these preliminary results, which are being confirmed by further experiments.

The Photo-synthesis of Nitrogenous Compounds and Nitrification

The photosynthetic utilisation of nitrogen by plants in the formation of proteins is in a large manner complementary to the production of carbohydrates from carbon dioxide and water. These substances equally with carbohydrates claim attention on account of their great importance as food materials. According to Baly and Barker, the photosynthesised formaldehyde is capable of reacting with ammonia or potassium nitrite to give complex nitrogenous compounds, i.e. amines, pyridine, quinoline bases, and alkaloids.

Snow and Stone[1] consider the evidence adduced by Baly as insufficient. Dhar and Sanyal have also been able to synthesise methylamine and an alkaloid from formaldehyde and ammonia exposed to tropical sunlight. It is believed that the proteins synthesised in the plants are produced in a similar manner.

Now as regards the source of plant nitrogen, it is generally believed that nitrites and nitrates, present in the soil, constitute the chief source of its

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[1] J. Chem. Soc., **123**, 1509 (1923).

supply. Moore and Webster[1] and Dhar and Sanyal believe that sunlight causes a slight union of nitrogen and oxygen in the formation of oxides of nitrogen, which are absorbed by the plants. The following experiments were carried on regarding the production of nitrogenous compounds in the plants and the nitrification process in the soil.

Experimental

A. *Photosynthesis of nitrogen compounds.*

As is generally believed and has further been carefully pointed out here that formaldehyde is first synthesised by the plants from carbon dioxide and water. Experiments were therefore made with 2% formaldehyde and ammonia using suitable photocatalysts.

Experiments	Time of exposure	Results
1. 2% HCHO with ammonia	24 hrs.	A small quantity of hexamethylene tetramine.
2. 2% HCHO with ammonia and TiO$_2$	30 hrs.	A large quantity of hexamethylene tetramine and a very small quantity of urethane but no urea, some nitrite.
3. 2%HCHO with ammonia and copper carbonate	30 hrs.	No urea, some nitrite, hexamethylene tetramine, and an oily substance which could not be identified being in very small quantity.
4. 2% HCHO with KNO$_3$	30 hrs.	some nitrite but no formhydroxamic acid.
5. 2% HCHO with ammonia and nickel carbonate	do.	hexamethylene tetramine.
6. Air free from nitrite fumes by passing through FeSO$_4$ solution was passed in conductivity water in a *Jena* glass beaker covered by a watch glass	3 hrs.	no nitrite.
7. The experiment (6) repeated by passing air free from nitrites in a *quartz* beaker covered with a quartz cover	2 hrs.	a very small quantity of nitrite detected.
8. 2% HCHO with ammonia and copper carbonate	16 hrs.	small quantity methylamine M.P. hydrochloride 95.9°C. and hexamethylene tetramine.

The tests employed to detect the compounds were those described by Plimmer in his "Practical Organic and Bio-Chemistry." The test for the nitrite was carried in the following way:

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[1] J. Chem. Soc., **119**, 1555 (1921).

A 0.5% solution of α-naphthylamine was prepared and another 1% solution of sulphanilic acid. 1 cc. of each solution was mixed and subsequently 10 cc. or 20 ccs. of the solution to be tested for nitrite were added. A similar blank containing pure conductivity water used in the experiments was also put up to compare the colour as the amount of nitrite produced was very small. On keeping the two beakers, a pink colour was developed in case when nitrite was present. This test is extremely sensitive and depends upon the well-known diazo-reaction with the nitrite formed.

Discussion of Results

Unequivocal evidence is brought forward for the formation of HCHO from CO_2 and water using numerous organic and specially inorganic catalysts. The chief inorganic catalysts used are $MnCl_2$, cobalt and nickel carbonates, copper sulphate, copper acetate and carbonate, chromium oxide, etc. All these are coloured substances having marked absorption in the visible spectrum. In the case of organic substances when used as a catalyst, the presence of formaldehyde has been attributed to the decomposition of the organic substances in sunlight. Experiments were conducted in which a solution of the organic photocatalyst was separately exposed to sunlight in which no carbon dioxide was passed. These solutions were distilled and the amount of formaldehyde detected. The presence of greater amounts of formaldehyde in the distillate in which carbon dioxide was passed clearly points out that the excess of formaldehyde is due to the photochemical reduction of carbon dioxide to formaldehyde. The amount of formaldehyde detected in presence of $MnCl_2$ used as a photocatalyst is 50 times greater than the limit to which the Schryver's test of formaldehyde used in this investigation is sensitive. One part of formaldehyde in 625,000 parts of water can be detected by this test. In the light of these experiments there is hardly any doubt that the presence of formaldehyde is due to its photoformation from CO_2 and H_2O. The production of only small amounts of formaldehyde has to be ascribed to the fact that the formaldehyde so synthesised being in the reactive state is polymerised to the reducing sugar. We are of the opinion that there are two simultaneous reactions occurring with the active formaldehyde:—

1. Reversion to inactive or ordinary HCHO.
2. Polymerisation into reducing sugars.

$$\text{Active formaldehyde}$$
$$\Updownarrow \qquad\qquad \Updownarrow$$
$$\text{Inactive formaldehyde} \rightleftarrows \text{Reducing sugars.}$$
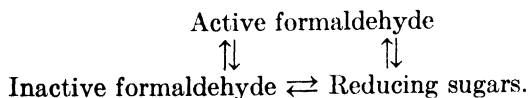
Baly and Barker differentiate this active formaldehyde from the ordinary variety by assigning to it a different structural formula. There is, according to the scheme, an equilibrium of the following type established in the process of photosynthesis:

$$\text{Active formaldehyde} \rightleftarrows \text{Reducing sugar}$$
$$\Updownarrow \qquad\qquad\qquad\qquad \Updownarrow$$
$$\text{Inactive formaldehyde} \rightleftarrows \text{Starch and other such products.}$$
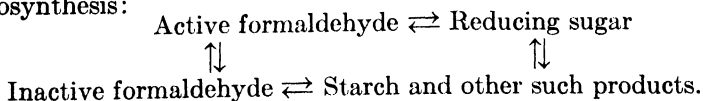
According to Bohr's conception of atomic structure an active molecule or a nascent molecule as popularly known, is characterised by possessing a higher energy i.e. being in a higher state of quantum orbit. Whether this nascent formaldehyde molecule is by itself capable of being polymerised with other active molecules to reducing sugar, without taking up any energy absorbed by the photocatalysts used, or this polymerisation of active formaldehyde into reducing sugars will also require a further supply of energy, is a question which is difficult to answer at this stage. Our knowledge of energy relations between the various stages is insufficient to enlighten upon this point. To throw light on this question, however, a study of the temperature coefficient of sugar synthesis from formaldehyde was undertaken.

In order to follow the arguments developed in this paper it will be worth while to consider some of the current views on this problem. From an analogy with these experiments in "vitro" it can be said with a certain amount of confidence that in the green plants too, the primary product of photosynthesis is formaldehyde which is polymerised to sugars. The reaction $CO_2 + H_2O \rightarrow HCHO + O_2$ takes place with an absorption of energy. The light energy absorbed by chlorophyll is in some way converted into chemical energy. On account of the readiness with which this photo-synthesised formaldehyde is polymerised into sugars, Baly and Barker have given it a different structural formula: $HCHO$ (ordinary) $\rightleftarrows HCOH$ (active). It is generally believed that chlorophyll plays the part of an optical sensitiser, but the mechanism of this sensitisation is not very clear. Spoehr[1] has stated that several authors incline to the view that the fluorescent property of chlorophyll may be the guiding factor in its capability to act as a sensitiser. In order to test this view, attempts were made by us to effect photosynthesis using different fluorescent organic dyes. A glance at the experimental results will at once make it clear that nearly all the fluorescent dyes used, failed to act as marked photosensitisers in the formation of formaldehyde. The efficiency of a fluorescent substance for photosensitisation will depend mainly upon three factors:—

(a) the amount of light absorbed by the fluorescent substance.

(b) the probability of activation of the molecules of the reactants on collision with these activated molecules of the fluorescent substances.

(c) the probability of the activated fluorescent molecule to decompose into some other products.

According to the newer conception of the quantised molecule, if a fluorescent molecule has absorbed less energy, it will not be in a sufficiently higher state of quantum orbit and hence the energy which this molecule can give to other reactant molecule in falling to a lower orbit will not be sufficient to activate a molecule like that of carbon dioxide which requires 120,000 calories for a gram mol to be activated for formaldehyde formation. Moreover, if the substance acting as photosensitiser has a great tendency to decompose into

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[1] "Photosynthesis" (1926).

other constituents, as was found notably in the case of fluorescein and carth-aramin and they were easily decolourised in light in three or four hours, there will not be sufficient chance of activation of a CO_2 molecule.

In the light of these negative results obtained with fluorescent substances, it appears that the fluorescent property of chlorophyll is not of much impor-tance in bringing about photosynthesis. It seems that this fluorescent property of chlorophyll helps all the more in its decolourisation when exposed to sunlight. Moreover the probability of activation of a CO_2 molecule will depend upon the intake of energy by the fluorescent chlorophyll molecule and this energy will be given out as a mono-chromatic radiation on its rever-sion to its original state. As CO_2 shows an absorption in the ultraviolet region, it cannot be possible for this molecule to be activated by this mono-chromatic radiation, which certainly will not be in the ultraviolet region. Thus it is quite clear that the marked photo-activity of chlorophyll has to be ascribed to properties other than fluorescence.

Weigert[1] advances the view that the absorption of light by chlorophyll results in an internal photo-electric effect, which results in the break-down of water into H_2O_2 and hydrogen, which react with carbon dioxide according to the following equation:—

$$H_2 + H_2O_2 + CO_2 \rightleftarrows HCHO + H_2O + O_2$$
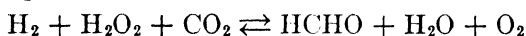
Besides these theories where an essentially physical significance is assigned to chlorophyll, there are some which give it an active part in the chemical reactions. Of these mention may be made of the theory of Willstätter and Stoll[2] who are of the opinion that carbonic acid forms a complex with chloro-phyll, which with absorption of energy passes into an isomeric peroxide type of compound. This breaks up thermally probably by the action of an enzyme with the formation of formaldehyde, oxygen, and regeneration of chlorophyll.

A modification of this theory of Willstätter and Stoll has been put forward by Gopala Rao and Dhar. They state that apart from all these properties of chlorophyll, it also exercises reducing properties to a certain extent. They have been able to demonstrate the reduction of CO_2 to CO in presence of chlorophyll when exposed to light. The CO was tested by the iodine pentoxide test. According to them photosynthesis consists of three stages:—

(a) In the first stage chlorophyll reacts with carbonic acid under the influence of light with the formation of chlorophyll peroxide and carbon monoxide.

(b) The nascent carbon monoxide reacts with water giving formaldehyde, and oxygen is evolved.

$$H_2O + CO \rightleftarrows HCHO + O$$
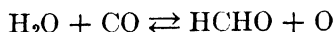
the other half of the molecule of oxygen comes from the decomposition of the chlorophyll peroxide and is probably thermal in nature and due to the enzyme present in the chloroplast.

(c) Polymerisation of this formaldehyde to sugars.

[1] Z. physik. Chem., **106**, 313 (1923).
[2] "Ûntersuchungen über Chlorophyll" (1913).

Thus oxygen evolution takes place in two stages, the one half being liberated in the action of carbon monoxide with water to form formaldehyde; the other half being liberated during the decomposition of chlorophyll peroxide. Gopala Rao and Dhar state that the photosynthetic activity is aided by the reducing action of chlorophyll, and that in the presence of a photocatalyst having reducing properties as well, formaldehyde formation is likely to be quicker and much facilitated.

Additional support to this theory has been given from the experiments described in this paper. It has been found that $MnCl_2$ and $FeSO_4$ give a larger amount of HCHO than the other insoluble powders. Baly and co-workers have stated that insoluble powders are the best catalysts for photo-synthesis. In view of this work of Baly, nickel, cobalt and copper carbonate and other insoluble powders mentioned in the experimental section were tried. No doubt they are good catalysts but $MnCl_2$ was found to be better than cobalt carbonate. The amount of formaldehyde was fifty times greater than the limit of sensitivity of the test. It seems to me that $MnCl_2$ and $FeSO_4$ apart from being photosensitisers exert reducing action, thus reducing some CO_2 to CO which easily forms formaldehyde. Why more formaldehyde is not detected with $FeSO_4$, is due to the fact that some of the $FeSO_4$ is oxidised, and the ferric salt so formed being an efficient converter of formaldehyde into sugars polymerises this formaldehyde at once.

The temperature coefficient of formaldehyde formation from CO_2 and water vapour in presence of $MnCl_2$ and chlorophyll was found to be nearly 1.5. This value of the temperature coefficient is greater than unity. But it is a well-known fact that purely photochemical reactions have their temperature coefficients nearing unity. It appears, therefore, that there are two stages in formaldehyde synthesis. One is the photochemical one and the other is the thermal process and hence the total process has a temperature coefficient greater than unity. Moreover, Miss Mathaei and Blackmann, Warburg and Willstätter have found that the temperature coefficient of photosynthesis in plant is greater than unity. Miss Mathaei and Blackmann have found that the temperature coefficient is as high as 2. This cannot certainly be characteristic of a photochemical reaction, but of thermal and enzymic reaction. The temperature coefficient will depend upon the slowest reaction. If the photochemical reaction is slow, the temperature coefficient will tend to be unity and if the thermal reaction is a slow one, the temperature coefficient will be higher. This behaviour has been well observed by Willstätter in the case of green and yellow varieties of the same species. The experimental results of Warburg on the relation between light intensity and temperature coefficient also support the new scheme of photosynthesis as advanced by us. All conditions remaining the same, the temperature coefficient is unity when the light intensity is low and the temperature coefficient is greater than unity when the light intensity is higher. In the first case, because the light intensity is low the photochemical reaction will be slow and will limit the whole process. When the intensity of light is high, the photochemical reaction will be sufficiently rapid and the thermal reaction will be slow and

hence the thermal reaction will limit the whole process. Thus from considerations already explained it is clear that in the former case, the process being limited by the light reaction and in the latter by the thermal reaction, the temperature coefficient in the former case will be smaller than in the latter.

Blackmann's principle of limiting factor which has been utilised in the discussion of the temperature coefficient has also shown that an internal factor like the content of chlorophyll with which carbon dioxide reacts is limiting the whole process. It was pointed out in an earlier part of this thesis that increase of carbon dioxide flow gave smaller amounts of formaldehyde, under similar conditions. This feature of the problem is also evident from Warburg's researches on the effect of carbon dioxide concentration, on the rate of photosynthesis. With increasing carbon dioxide concentration above a certain limit Warburg found that the increase in the rate of photosynthesis rapidly falls off, until a certain concentration of CO_2, further increase in the latter produces no effect. According to this hypothesis CO_2 reacts with chlorophyll as follows:

Chlorophyll + carbon dioxide + water.
= chlorophyll peroxide + CO.
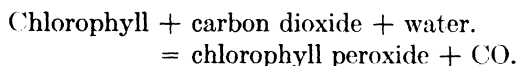
At low concentrations of CO_2 when chlorophyll is in comparatively greater quantities, it is clear that the photosynthesis will increase with increasing concentration of CO_2. But this will not increase *ad infinitum*. The content of chlorophyll being limited, a certain stage will be reached where the content of chlorophyll is no longer in excess but is just sufficient to interact with the carbon dioxide present at any instant, if the concentration of carbon dioxide is further increased there will be no further increase in the reaction velocity, as the chlorophyll with which carbon dioxide interacts is in limited quantities. The extra carbon dioxide finds no chlorophyll to react with, hence no photosynthetic increase with increase of carbon dioxide concentration is observed.

Polymerisation of Formaldehyde to Sugars

The results obtained with such experiments are interesting and lead to important conclusions regarding the mechanism of the polymerisation of formaldehyde to sugars and ultimately to the mechanism of photosynthesis.

Solution of formaldehyde exposed to light is not polymerised to sugars when it is exposed to sunlight but if a formaldehyde solution is exposed with catalysts like $FeCl_3$ and chlorophyll, a sure and distinct test for reducing sugars is obtained. Thus it is quite clear that in presence of chlorophyll, formaldehyde can be polymerised to reducing sugars by using the energy absorbed by chlorophyll. The yield of sugars, however, is not so great as to account for the large photosynthetic activity going on in the plants. But it should not be concluded from this that formaldehyde cannot form the first stage in the process of photosynthesis. There is an essential difference in this formaldehyde used in the laboratory and the formaldehyde synthesised in the plants. The formaldehyde synthesised is in a nascent state when it is

just formed and thus possesses a great store of energy. This stored energy in nascent formaldehyde makes a formaldehyde molecule capable of being polymerised into sugars. From the fact that a large amount of energy is needed for the polymerisation of ordinary formaldehyde to reducing sugars, it is quite apparent that a nascent molecule of formaldehyde must be in possession of a large amount of stored energy. The results with ferric chloride and chlorophyll leave no doubt as to the validity of the statement that formaldehyde even in the ordinary condition is capable of being polymerised into reducing sugars.

The experiments on the temperature coefficient of formaldehyde formation are interesting and point out clearly that the polymerisation of formaldehyde into reducing sugars is essentially a photochemical process because the temperature coefficient between 30 to 40°C is nearly unity and this is a characteristic of the truly photochemical reactions. Baly,[1] however, has stated that the photosynthetic activity falls in "vitro" at about 31°C and in plants above 36°C. These results of Baly in "vitro" are not corroborated by our observations. Further work will explain the difference between our results and those of Baly.

It is difficult to state definitely whether nascent formaldehyde itself polymerises to sugars or requires an extra amount of energy to be polymerised. It is very likely that the polymerisation of formaldehyde into reducing sugars might be taking place in two stages. First the formaldehyde molecule simply polymerises into a substance having a formula $(HCHO)_n$ and then this is transformed by an intra molecular change into glucose or other sugars, as the case may be. Our experimental results show definitely that ferric salts and chlorophyll are efficient photocatalysts in the polymerisation of formaldehyde to reducing sugars.

Oxidation of Ammonia and its Compounds to Nitrate

Dhar and Sanyal have shown that ammonia solution can be slightly oxidised to nitrate by passing air when exposed to light. Gopala Rao and Dhar have shown that the velocity of oxidation can be greatly increased by adding some photo-sensitisers like titanium dioxide, zinc oxide, cadmium oxide, etc. They have further shown that ammonium sulphate, chloride, carbonate and phosphate can also be oxidised. Similarly on the basis of these experiments they have given out the view that the nitrification in soils is at least partly photochemical taking place at the surface of various photocatalysts present in the soil in the presence of sunlight. They have shown that this theory is capable of explaining many facts inconsistent with the bacterial theory of nitrification.

The present authors have now shown that ammonium oxalate, tartrate, and formate can similarly be oxidised though much less than the inorganic salts. They have shown that the rate of oxidation is greater in the March sun than in the January sun.

[1] Nature, October 25 (1930).

Summary

1. The polymerisation of formaldehyde to reducing sugars has been effected by light in the presence of ferric chloride, chlorophyll, nickel carbonate, methyl orange and zinc oxide. Of these ferric chloride is the best photochemical polymerising agent.

2. The temperature coefficient of the polymerisation of formaldehyde to reducing sugars has been found to be 1.1 for a rise of 10 between 30 and 40.

3. A few cases of the photosynthesis of nitrogenous compounds has also been reported.

4. A discussion of the results of Part III and IV is presented.

Chemical Laboratory,
University of Allahabad,
Allahabad, India.
June 4, 1931.

RAMAN EFFECT IN INORGANIC COMPOUNDS

BY J. C. GHOSH AND S. K. DAS

Since the discovery of the Raman effect,[1] which has opened up a new method of investigating molecular spectra in the infra-red region, several organic and inorganic substances have been studied with the object of interpreting the frequency shifts in Raman spectra in terms of their constitution.

The correlation of Raman shifts with the characteristic oscillation frequencies and molecular constitution in organic compounds has chiefly been carried out by Dadieu and Kohlrausch, Venkataswaran and Ganesan, Petrikaln and Hochberg and others and the results they have obtained are of far reaching importance.

The correlation of frequency shifts in inorganic compounds with the grouping of atoms and their characteristic oscillation frequencies was first brought about by the works of Rosen, Pringsheim and Carelli[2] on several inorganic nitrates in solution. A single shift 1046 cm^{-1} was obtained corresponding to the inactive frequency of the $NO_3{}^-$ ion, assuming the arrangement to be an equilateral triangle with the nitrogen atom at the centre and the three oxygen atoms at the three corners.

The same results have virtually been obtained by Gerlach. Kinsley, Bell, Frederickson, Williams, Nishi, Krishnamurthi, Ramaswamy, Rao[3] and others, the latter measuring electrolytic dissociation by Raman methods. In each case the inactive frequency appeared brightest and the shifts were uninfluenced by the nature of the cation. The inactive frequencies of those which do not produce any change in the electric moment of the group do not appear in the infra-red absorption and hence the discovery of the Raman effect, where such inactive frequencies appear strongly, enables an exact determination of all the fundamental frequencies of simple atomic groups.

Dillon and Dickinson's[4] experiments on ionised substances of allied chemical character revealed that the frequency shift is in some cases independent of the number of oxygen atoms associated with the central atom, and further, the frequency change of the line due to inactive frequency decreases with the increase of atomic number of the central atom of the anion. A further suggestion is offered to interpret the frequency shift as a measure of the stiffness of binding.

The present paper deals with certain well-defined groups of inorganic compounds in solution, the Raman shifts being interpreted in terms of characteristic oscillation and molecular constitution. How far the suggestion of Dillon and Dickinson holds good in the above cases, can be observed from the results obtained.

[1] Indian J. Phys., **2**, 389 (1928).
[2] Z. Physik, **51**, 511 (1928).
[3] Proc. Roy. Soc., **127A**, 279 (1930).
[4] Proc. Nat. Acad. Sci., **15**, 334 (1929).

Experimental

Substances soluble in water were used in state of solution. The substances were all of Kahlbaum's or Merck's preparation (Extra Pure), further purified if necessary. A saturated solution was made with re-distilled water and was rendered free from any suspended matter by repeated filtration.

The method of illumination was virtually the same as that of Wood.[5] The solution was put in an inner tube placed inside a vertical outer jacket, through which water was circulated, substituted by colored solution when necessary. The whole arrangement was clamped upright and a vertical quartz mercury-lamp is placed along-side, so that the light scattered at right angles, emerges along the axis of the vertical tube. This scattered beam is totally reflected by a rectangular prism into the slit of the spectrograph thereby making the maximum illumination available. The slit of the spectrograph was shielded from direct illumination by suitable screens and practically the whole of the light that entered the spectrograph was due to scattering at right angles.

With this arrangement, using soft-gradation panchromatic plates (Backed), H & D 2000, and a Fuess constant deviation glass spectrograph (the investigations being carried out in the visible region of the spectrum) an exposure of four to six hours was found to give satisfactory spectrogram. Appearance of fainter details required longer exposures.

The plates were all measured with a Hilger travelling micrometer, and the wave-lengths of the lines calculated by using the simplified form of Hartman's interpolation formula ($\lambda = \lambda_0 + c/(n-n_0)$) with the known mercury lines appearing on the plates as standards. The wave-numbers of the lines (in vacuo per cm.) were then calculated and the shift in wave-numbers of the Raman lines from the corresponding exciting lines determined.

Results and Their Discussions

It is well known that in solutions of strong electrolytes we have complete dissociation into ions and the Raman lines observed for such solution must be ascribed to the ions in the solution. In the following pages the Raman lines of polyatomic ions in the order of their increasing molecular complexity will be discussed. The simplest elementary ions have not yet been found to give Raman shifts.

A. *Raman lines due to diatomic ions:*—The investigations of Pal and Sen Gupta[6] show that the CN' ion in KCN gives a single Raman line 2080 cm^{-1}. This frequency due to the CN' ion is much less than the frequency observed when CN' group forms part of a more complex ion like OCN' ($\Delta\nu = 2183$) or of a non-ionisable compound like CH_3CN ($\Delta\nu = 2256$).

We have always failed to obtain any Raman shift for the OH' ion though Woodward[7] claims to have observed the shift, $\Delta\nu = 3615 \pm 25$ cm.$^{-1}$

[5] Phil. Mag., **6**, 729 (1928).

[6] Indian J. Phys., **5**, 612 (1930).

[7] Woodward: Physik. Z., **32**, 261-262 (1931).

A solution of sodium hydrogen sulphide, a strong electrolyte, obtained by passing H_2S gas through caustic soda solution and removing free H_2S by air, gave a Raman line 22130 cm^{-1}. The Raman shift 2575 cm^{-1} is the same as has been observed in liquid H_2S and in various mercaptans.[8] The behaviour of SH' ion is therefore unlike that of CN' ion in that the Raman shift is independent of the manner in which the other valency of sulphur atom is saturated.

B. *Raman lines due to triatomic ions:*—The Raman shifts due to sodium metaborate ($NaBO_2$) and sodium nitrite solutions[9] are given in Table I.

TABLE I

| $NaNO_2$ | 696 cm^{-1} | 785 cm^{-1} | 1303 cm^{-1} |
| $NaBO_2$ | 253 cm^{-1} | | 1403 cm^{-1} |

In a symmetrical linear model like CO_2, CS_2, $HgCl_2$ we generally have a strong Raman line representing the symmetrical inactive vibration of the terminal atoms against the central atom, with a faint companion. Thus CO_2 has a strong line $\Delta\nu = 1284$ cm^{-1} with a very weak companion $\Delta\nu = 1392$ cm^{-1}, CS_2 and $HgCl_2$ give strong lines $\Delta\nu = 655$ cm^{-1} and 312 cm^{-1} with weak companions $\Delta\nu = 795$ cm^{-1} and 381 cm^{-1} respectively.

A non-linear model, however, according to Bhagavantam[10] should reveal three independent oscillation frequencies. In the case of SO_2 this is actually observed. The NO_2' ion gives three independent oscillation frequencies $\Delta\nu = 696$ cm^{-1}, 785 cm^{-1}, 1303 cm^{-1}, in the case of BO_2' ion two such frequencies have actually been observed, $\Delta\nu = 253$ cm^{-1} and 1403 cm^{-1}, the third line being perhaps too faint to be detected. Hence both these ions should be represented by a non-linear model.

It is interesting to note that unlike the case of SH group, the Raman frequency due to NO_2 group does not remain constant. Thus in nitrobenzene the Raman shift observed is 1342 cm^{-1} as against 1303 cm^{-1} in sodium nitrite solution.

We may include in this category the hypophosphite ion, though it is not triatomic. The hydrogen and oxygen atoms however, in this ion, so far as Raman effect is concerned behave as two hydroxyl groups with the probable constitution $P(OH)_2'$. This is of course, not in harmony with the accepted chemical constitution of this ion.

TABLE II

Sodium hypophosphite

Frequency Shift	Intensity
1080	2
952	1

We have two lines of comparable intensity $\Delta\nu = 952$ cm^{-1} and 1080 cm^{-1} analogous with the lines $\Delta\nu = 795$ cm^{-1} and 1303 cm^{-1} for the nitrite ion.

[8] Bhagavantam: Nature, **126**, 502 (1930); Venkataswaran: Indian J. Phys., **5**, 223 (1930).
[9] Z. Physik, **51**, 511 (1928).
[10] Indian J. Phys., **5**, 81 (1930).

In agreement with the views of Dillon and Dickinson, we find that the frequency shift diminishes as the central atom in the ion becomes heavier. Thus we have for:—

BO_2^-	NO_2^-	$P(OH)_2^-$
Frequency Shifts 1403 cm^{-1}	1303 cm^{-1}	1080 cm^{-1}

In the case of other triatomic ions, where the atoms are all different from one another, we have two characteristic frequency shifts due to the two valency bonds, e.g. in SCN ion, we have besides 2080 cm^{-1} due to $-C=N$, another shift 740 cm^{-1} due to $S-C$ bond.[11]

C. *Ions of the type* XO_3:—This type of ion has already been investigated and the general character of the Raman shifts exhaustively described.[12]

A few gaps however remain to be filled up—e.g. PO_3', VO_3' and AsO_3''' (metaphosphate, metavanadate and arsenite) ions which are very similar to NO_3', being ions of oxy-acids of elements in the same group of the periodic table, do not appear to have been investigated.

<div align="center">TABLE III</div>

Sodium nitrate[13]	726 cm^{-1}	1048 cm^{-1}
Sodium metaphosphate		1137 cm^{-1}
Sodium metavanadate	228 cm^{-1}	367 cm^{-1}
Sodium arsenite	144 cm^{-1}	203 cm^{-1}

In sodium metaphosphate we have been able to observe only one Raman shift 1137 cm^{-1}. It may be observed here that viscous liquids do not as a rule give conspicuous Raman lines. We rather meet with general scattering, due perhaps, to the considerable forces, which neighbouring molecules exert on one another.

The Raman shifts of VO_3' ion are similar to those of NO_3' ion. In fact we have the curious coincidence that the ratios of $\dfrac{726}{228}$, $\dfrac{1048}{367}$, and $\dfrac{23(\text{At. No. of V})}{7(\text{At. No. of N})}$ have approximately the same value. Comparing NO_3' with AsO_3''' ion we find again that the ratios $\dfrac{726}{144}$, $\dfrac{1048}{203}$ and $\dfrac{35(\text{At. No. of As})}{7(\text{At. No. of N})}$ are approximately the same. Thus for similarly constituted ions containing several atoms of oxygen, the ratio of the comparable Raman shifts is inversely as the atomic number of the central atom.

D. *Ions of the type* XO_4:—Investigations of this type of salts have been carried out by Krishnamurthi[14] and Nishi.[15]

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[11] Krishnamurthi: Indian J. Phys., 5, 654 (1930).

[12] Leontowitsch: Z. Physik, 54, 155 (1929); Gerlach: Nature, 1930, 819; Nishi: Mem. Coll. Sci. Kyoto, 13A, 163 (1930); Krishnamurthi: Indian J. Phys., 5, 633 (1930).

[13] Ramaswamy: Indian J. Phys., 5, 200 (1930).

[14] Indian J. Phys., 5, 633 (1930).

[15] Jap. J. Phys., 5, 119 (1929).

We have not been able to observe any Raman line for solutions of Na_3PO_4, but for solutions of arsenates Na_3AsO_4 and orthovanadates Na_3VO_4, Raman lines have been observed. It may be mentioned here that orthovanadates are formed by the addition of alkali to metavanadates and we find accordingly a complete change in the Raman spectra by progressive addition of hydroxyl ion to metavanadate solution. Thus for metavanadate we have Raman shifts of 228 and 367 cm^{-1} while for orthovanadate, we have Raman shifts of 880 and 907 cm.$^{-1}$

TABLE IV

AsO_4'''	349 cm^{-1}	462 cm^{-1}		
VO_4'''			880 cm^{-1}	
			907 cm^{-1}	
SO_4''[13]	457 cm^{-1}	617 cm^{-1}	981 cm^{-1}	1102 cm^{-1}
S_2O_8''			833 cm^{-1}	1081 cm^{-1}

Here also we find the qualitative relationship that as the atomic number of the central atom increases the corresponding Raman shifts become less. The comparable Raman frequencies in persulphate ion have smaller values than those of sulphate ion.

Ammonium molybdate and sodium tungstate solutions give a large number of Raman lines and the spectra appears to be similar in nature.

TABLE V

MoO_4'''	256 cm^{-1}	356 cm^{-1}	879.8 cm^{-1}	932.4 cm^{-1}		
WO_4''		371 cm^{-1}	925 cm^{-1}	1017 cm^{-1}	1540 cm^{-1}	1394 cm^{-1}

If, however, to sodium tungstate solution we add hydrochloric acid so as to obtain a tungstic acid sol Raman lines become very faint. Several other acid sols like silicic acid, molybdic acid have been tried in this laboratory, but no Raman lines could be detected. It appears that colloidal solutions and amorphous solids cannot be easily stimulated to yield Raman radiations.

E. *Acids and acid salts of the type* $H_3PO_3, NaH_2PO_3, Na_2HPO_3, NaHSO_3$:— These have been investigated and show considerable similarity in behaviour.

TABLE VI

H_3PO_3	672 cm^{-1}	940 cm^{-1}	1012 cm^{-1}	
NaH_2PO_3	642 cm^{-1}	925 cm^{-1}	1068 cm^{-1}	
Na_2HPO_3	—	980 cm^{-1}	1030 cm^{-1}	
$NaHSO_3$	346 cm^{-1}	826 cm^{-1}	963 cm^{-1}	1406 cm^{-1}

The Raman lines of phosphorous acid and sodium dihydrogen phosphite are almost identical, the lines being really due to H_2PO_3' ion. The ions HSO_3' and HPO_3', give analogous Raman lines. It may be mentioned here that the Raman spectra of liquid SO_2 ($\Delta\nu = 526$ cm^{-1}, 1146 cm^{-1} and 1340

cm^{-1}) are completely different in nature from those of HSO$_3$' ion, thus indicating a considerable change in the molecular structure of SO$_2$ gas when dissolved in alkali.

In Table VII are given the wave-lengths, the corresponding frequencies expressed as wave-numbers per cm. in vacuum and the notations of the exciting mercury lines.

Tables VIII-XXIII show the wave-numbers in vacuum per cm. of the modified lines, their intensity and the corresponding exciting lines.

TABLE VII

In I.A.	43583	404656
In cm^{-1}	22938	24705
Notations	a	b

TABLE VIII

Sodium Hydrogen Sulphide

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22130	5	b—2575

TABLE IX

Sodium Metaborate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23302	3	b—1403
22685	1	a—253

TABLE X

Sodium Nitrite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22342	2	a— 696
22153	1	a— 785
221635	5b	a—1303

TABLE XI

Sodium Hypophosphite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23628	2	b—1077
21856	2	a—1082
21986	1	a— 952

TABLE XII

Sodium Metaphosphate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23570	1	b—1135
21799	2	a—1139

TABLE XIII

Sodium Metavanadate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22710	1	a—228
22571	1	a—367

TABLE XIV

Sodium Arsenite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22794	1	a—144
22735	1	a—203

TABLE XV

Sodium Arsenate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22589	1	a—349
22476	2	a—462

TABLE XVI

Sodium Orthovanadate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23823	2b	b—882
22064	1	a—878
23798	2b	b—907

TABLE XVII

Sodium Persulphate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23871	3	b— 834
22105	4	a— 833
23621	3	b—1084
21857	4	a—1081

TABLE XVIII

Ammonium Molybdate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
22008	4	a—930
23769	4	b—936
220582	1	a—879.8
22682	1	a—256
22582	1	a—356

TABLE XIX

Sodium Tungstate

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23168	2	b—1537
21375	2	a—1543
23780	2	b— 925
22008	2	a— 930
21544	1	a—1394
21921	1	a—1017
22567	2	a— 371

TABLE XX

Phosphoric Acid

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23764	4	b— 944
22002	4	a— 936
23692	2	b—1012
21926	2	a—1013
22265	5b	a— 672

TABLE XXI

Acid Sodium Phosphite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23639	2	b—1066
21868	4b	a—1070
22013	2	a— 925
22296	4b	a— 642

TABLE XXII

Normal Sodium Phosphite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23727	3	b— 978
23678	1	b—1027
21956	3	a— 893
21905	1	a—1033

TABLE XXIII

Sodium Hydrogen Sulphite

Wave-number of R (vac) per cm.	Intensity	Exciting line and frequency shift
23299	2	b—1406
22592	0	a— 346
22112	0	a— 826
21975	1	a— 963

Chemical Laboratory,
Dacca University,
India,
September 17, 1931.

ON THE PREPARATION OF UPPER LIQUIDS PRODUCING SATIS-FACTORY BOUNDARY CONDITIONS IN CATAPHORETIC MEASUREMENTS AND THE UNCERTAINTIES OF THE USUAL MEASUREMENTS OF CATAPHORETIC SPEED

BY JNANENDRA NATH MUKHERJEE

The errors inherent in the procedure of Burton, who following Whetham used equiconducting solutions as the upper layer for producing the boundary without reference to the changes brought out by ionic migrations across it, have been discussed in detail.[1] An improved but more complicated method rectifying these defects has been described.[2] The defects pointed out in these papers have been confirmed by Freundlich and Zeh,[3] and by Kruyt,[4] and by Kruyt and Willigen.[5] It appears (see the remarks of Freundlich: "Kapillarchemie" (1930); and of Pauli and Valkò: "Elektrochemie der Kolloide" (1929) that the theoretical considerations underlying the writer's method have been somewhat overlooked. No attention is paid in most investigations with the boundary method to *determine experimentally the suitability of a given liquid for producing satisfactory boundary conditions.*

Theoretical Considerations

Kohlrausch[6] states that the boundary between two electrolytes AR and BR with a common ion R—in case the faster moving ion is followed by the slower moving ion—can be assumed to be stable when the relation $C_A/N_A = C_B/N_B$ ..... (1) holds: C_A, C_B and N_A, N_B are respectively the concentrations and transport numbers of the two ions A and B. Ohm's law is assumed to be valid and the two ions move at the same speed under these conditions. Further if the concentrations are not as above they will adjust themselves so as to secure the above relationship at the boundary. In practice such an adjustment seldom occurs.[7] The ratio of the movements of the ions A and R, when they move into a column AR and are followed respectively by the slower moving ions B and R', is however constant. *That is, even when equation (1) is satisfied the movement of the boundary cannot be utilised for the measurement of the absolute rate of migrations.* This happens because at the boundary between AT and BR an unequal transfer of ions of opposite signs of magnitude given by the following expression takes place.[8]

[1] Mukherjee: Proc. Roy. Soc., 103A, 102 (1923); J. Indian Chem. Soc., 5, 593 (1928).

[2] Mukherjee: Proc. Roy. Soc., loc. cit.; J. Indian Chem. Soc., 2, 296 (1925).

[3] Z. physik. Chem., 114, 84 (1925).

[4] Kolloid-Z., 34, 358 (1928).

[5] Kolloid-Z., 44, 22 (1928).

[6] Kohlrausch: Wied. Ann., 62, 209 (1897); see also Weber: Sitzungsber. Akad. Wiss. Berlin, 1897, 935.

[7] McInnes: J. Am. Chem. Soc., 45, 2246 (1923); 46 1398 (1924); 41 994, 1009 (1919); 49, 1710 (1927).

[8] Mukherjee: J. Indian Chem. Soc., 5, 593 (1928).

$$- i \left| (N_R)^{BR} - N_R)^{AR} \right| \frac{dx}{P_{BR} \cdot V_R} \quad \dots\dots\dots\dots (2)$$

where i denotes the current density, $(N_A)^{AR}$ is the transport number of the ion R in the electrolyte AR, dx is the thickness of the layer of electrolyte BR into which the ions coming from the layer AR will spread during the interval dt. $P_{BR} \cdot V_R$ is the actual speed of the ions R in the layer BR and V_R is the mobility of the ion R per unit potential gradient.

The boundary method would thus appear to have no theoretical sanction.[1] *It however constitutes the most suitable one (see later) and it is possible definitely to lay down the theoretical requirements for reliable measurements by this method.*

There will be no electric drag (vide eq. 2) when the transport numbers are equal. This can happen when the two ions A and B have the same rate of migration (under unit potential gradient). If the mobility of the ion R is very great compared to that of A or B its transport number will be *nearly* the same for both electrolytes. Colloidal solutions generally contain free electrolytes in the intermicellary liquids even in dialysed sols. This makes it possible to realise satisfactory theoretical conditions. *In order that the movement of the boundary correctly indicates the true rate of migration it is evident that the electrical drag, resulting from unequal transfers of ions of opposite sign as also from differences in specific conductivity resulting from changes in concentration, should not be produced by the movement of the boundary. The upper liquid must therefore be*[2] *(1) an equiconducting solution and (2) it must in addition secure a uniform ionic environment.* If the colloidal solutions contain the positive carriers of electricity K_1, K_2, K_3 etc., and the negative carriers A_1, A_2, A_3 etc., having respectively the concentrations C_{k_1}, C_{k_2} ...... and C_{A_1}, C_{B_2} ..... and the rates of migrations U_{k_1}, U_{k_2} .... and V_{A_1}, V_{A_2} ..... then the upper liquid should also have a set of carriers K_1', K_2', K_3' .... and A_1', A_2', A_3' ... such that their equivalent concentration and rates of migration (under unit potential gradient) correspond exactly with that of K_1, K_2, K_3 .... and A_1, A_2, A_3 ... *That these conditions are satisfied can be verified experimentally* as (a) the potential gradient across the boundary will remain constant during both the upward and downward movements and (b) the rate of migration will be the same for both movements provided the particles have no appreciable rate of settling.[3] *Condition (b) signifies the absence of a different potential gradient stretching over small layers at the boundary arising out of ionic migrations disturbing the boundary.* The following other conditions should be ensured: (3) the specifically lighter solution should be at the top of the heavier one[4]

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[1] The conditions for measuring the rate of migration from the movement of the boundary between AR and BR are being investigated and the preliminary results have been communicated for publication.

[2] Mukherjee: J. Indian Chem. Soc., **5**, 593 (1928).

[3] An apparent rate of settling sometimes results from the migrations across the boundary and the inconstancy of the potential gradient as also from a difference of the level of the colloid in the two limbs of the U-tube (J. Indian Chem. Soc., **5**, 735 (1928); S. N. Mukherjee: Kolloid-Z., **52**, 63 (1930)).

[4] Steele: Z. physik. Chem., **40**, 689 (1902).

(4) ions in crossing from one side of the boundary to the other should not react to form undissociated molecules, precipitates or complex ions so as to change the nature of the electrolytes on the other side;[1] (5) the products of electrolysis should affect as little as possible the composition of both sides of the boundary;[2] (6) the heating effects of the current should be negligible;[3] (7) the colloid on the two limbs of the U-tube should be on the same level; (8) the error in calibrating the effective distance between the two lowest marks of the U-tube should be avoided. This error is considerable for sols of low conductivity and possibly arises out of the irregular distribution of the lines of force round the electrodes placed in the limbs of the tube for the calibration. The calibration should be made with fairly conducting solutions and the electrodes placed in vessels attached to the limbs of the U-tube during measurement of the cataphoretic speeds.[4] Reference should be made to the recent observations of Buchner and van Royen.[5] They find that differences in conductivity are responsible for the spreading effect of an electric field on boundaries between two electrolytes. This corroborates the preceding remarks as also what has been realised by earlier workers on the absolute migration of ions (e.g., Whetham).

The Suitability of the Ultrafiltrate as the Upper Liquid

The ultrafiltrate of the sol has been used as the upper liquid. In most measurements it has a different specific conductivity than that of the colloid, and the potential gradient in the colloid column is calculated from known specific conductivities and the lengths occupied by the two liquids in the U-tube. The preceding considerations will show that Ohm's law is not applicable in the case of such a boundary. Besides the ultrafiltrate has not always the same composition as the intermicellary liquid. These difficulties will vitiate the results obtained with the ultrafiltrate as the upper liquid and will be greater the smaller is the concentration of intermicellary electrolytes and the greater the Donnan effect during ultrafiltration (see later). On the other hand Freundlich[6] has pointed out that upper liquids containing ions not present in the sol are likely to alter the charge carried by the colloidal particles of the pure sol. It is however possible in most cases to use an upper liquid containing no foreign ions and satisfying the theoretical requirements. At any rate a separate investigation must be carried out to determine the suitability of any given electrolyte as the upper liquid. Where foreign ions are present in the upper liquid it can be experimentally tested how far they influence the charge and which of the two procedures gives the more correct results (see later). The following experimental observations illustrate the unsuitability of the ultrafiltrate as an upper liquid.

[1] Miller: Z. physik. Chem., **69**, 436 (1909).

[2] Mukherjee: J. Indian Chem. Soc., **2**, 298 (1925).

[3] Mukherjee: J. Indian Chem. Soc., **4**, 493 (1927); S. N. Mukherjee: Kolloid-Z., **52**, 63 (1930).

[4] Mukherjee: J. Indian Chem. Soc., **4**, 493 (1927).

[5] Kolloid-Z., **49**, 249 (1929).

[6] Z. physik. Chem., **114**, 84 (1925).

Ferric hydroxide sol (experiments by Mr. M. M. Biswas: sol contains .0143 moles Fe_2O_3 per litre; pH after coagulation by solid K_2SO_4 = 2.0).

The specific conductivities and the concentrations of the total chlorine and the chlorine ion activities are given for the (I) colloidal solution (II) its ultrafiltrate (III) the residual sol after ultrafiltration and (IV) the supernatant liquid after coagulation by potassium sulphate (solid). The results indicate the changes brought about by ultrafiltration.

TABLE I

Soln.	Sp. Conductivity	Cl. ion concentration	Total chloride concentration
I	.002563	.006985 N	.008588 N
II	.002165	.005761 N	.005932 N
III	.002480	.007408 N	.01554 N
IV	—	.007408 N	.00777 N

The chlorine ion concentration was determined by Ag/AgCl electrodes and the total chlorine by electrometric titration in nitric acid with silver nitrate. The ultrafiltrate was obtained with collodion filters using a nickel-plated ultrafilter (Zsigmondy pattern).

The cataphoretic speeds (cm. per sec. per volt per cm. $\times$ 10^5) and the potential gradients with the ultrafiltrate as the upper liquid are given below.

TABLE II

Sol contains .0143 moles of Fe_2O_3 per litre; pH = 2.00

Upward			Downward		
Pot. grad. before cataphoresis	Pot. grad. after cataphoresis	Cataphoretic speed	Pot. grad. before cataphoresis	Pot. grad. after cataphoresis	Cataphoretic speed
1.054	1.009	38.77	1.017	1.075	54.13
1.035	.9895	40.62	1.022	1.080	51.81

The ultrafiltrate thus does not at all give a satisfactory boundary. It may be mentioned that the percentage difference in the potential gradient depends on the length of the column of liquid over which the potential drop is measured. In this tube the distance is considerable. Shorter distances and simultaneous measurements of the potential gradient in the colloid layer, in the upper liquid and in a layer containing the boundary are desirable in many cases.[1]

The following procedure was ultimately adopted for obtaining a suitable upper liquid. The sol was coagulated with a few drops of a concentrated solution of potassium sulphate and the pH[2] of the supernatant liquid after coagulation was determined colorimetrically. A solution of hydrochloric acid having the same pH was prepared. It was made equiconducting with the sol. For this purpose to about 500 cc. of the solution the requisite quantity (a few drops) of a saturated solution of ferric chloride was added. The upper liquid

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[1] Mukherjee: Proc. Roy. Soc., **103A**, 102 (1923).

[2] This is not necessarily the same as that of the intermicellary liquid.

thus obtained was found to be satisfactory. Hydrochloric acid solutions of slightly higher pH were found to be more satisfactory, possibly the addition of ferric chloride lowers the pH. The results are given in Tables III and IV.

TABLE III

Pure Sol A; pH = 3.2; 0.042 moles of Fe_2O_3 per litre

Equicon-ducting upper liquids	Upward			Downward		
	Pot. gradient		Cataphoretic Speed per sec.	Pot. gradient		Cataphoretic Speed per sec.
	Before	After		Before	After	
KCl	0.661	0.647	29.2	0.573	0.900	87.2
LiCl	0.709	0.707	16.8	0.688	0.860	88.0
KCl in .001N HCl	0.678	0.694	26.6	0.662	0.878	50.8
HCl	0.552	0.775	46.4	0.767	0.460	44.0

TABLE IV

Pure Sol B; pH = 2.9; 0.0342 moles of Fe_2O_3 per litre

Equicon-ducting upper liquids	Upward			Downward		
	Pot. gradient		Cataphoretic Speed per sec.	Pot. gradient		Cataphoretic Speed per sec.
	Before	After		Before	After	
HCl	0.647	0.817	56.5	0.796	0.682	50.2
LiCl in .001N HCl	0.765	0.790	37.7	0.737	0.859	52.8
LiCl	0.590	0.586	32.5	0.586	0.776	63.6
FeCl₃ in .001N HCl	0.707	0.764	44.2	0.773	0.704	47.4
FeCl₃ in .00067N HCl	0.671	0.671	53.4	0.675	0.673	49.5

S. N. Mukherjee observing with great care obtained a very satisfactory agreement:

TABLE V

(Cp. S. N. Mukherjee: Kolloid-Z., 52, 64 (1930)).

(The Sol A contains .0295 gm. moles of Fe_2O_3 per litre)

Date of measurement:	Dilution	pH	Cataphoretic speed		Mean value
			Upward	Downward	
15.3.29	0	4.5	60.2	59.7	60.9
16.3.29	0	4.5	60.3	58.9	59.6
15.4.29	0	4.6	57.8	58.2	58.0
13.3.29	2	4.9	61.7	60.7	61.2
17.3.29	2	4.9	63.9	62.6	63.2
16.4.29	2	5.0	61.7	58.2	59.9
14.3.29	4	4.9	76.4	75.1	75.7
17.4.29	4	5.0	74.1	75.2	74.7
18.4.29	5	5.2	60.4	59.9	60.2
19.4.29	10	5.3	55.3	54.9	55.1

Copper Ferrocyanide Sol

Fresh observations with copper ferrocyanide sol by Mr. S. G. Choudhury and by Mr. K. P. Chatterjee are given below:

The sol was prepared by washing repeatedly a precipitate[1] of copper ferrocyanide with pure water till the mass peptised. Table VI shows the irregular results obtained with the ultrafiltrate and the other equiconducting electrolytes:

TABLE VI

N. P. Chatterjee

Date	Dilution of sol	Electrolyte used in the upper liquid	Sp. conductivity of sol at 28°C±2°	Pot. gradient[2]				Cataphoretic Speed	
				Upward		Downward			
				Before	After	Before	After	Upward	Downward
18.2.31	1:1	$K_4Fe(CN)_6$	1.8×10^{-5}	1.4	1.4	2.16	2.18	19.6	15.3
20.2.31	1:1	KCl	1.8×10^{-5}	1.5	1.5	2.5	2.5	21.1	11.3
11.3.31	1:1	KOH	4.3×10^{-5}	.81	.86	1.2	1.2	27.2	18.9
12.3.31	1:3	HCl	2.5×10^{-5}	.68	.59	1.2	1.2	34.9	16.6
13.3.31	1:3	$CuCl_2$	2.5×10^{-5}	.93	.95	1.0	1.1	18.3	Diffuse boundary
18.3.31	1:7	Ultrafiltrate	1.6×10^{-5}	.63	.65	1.4	1.4	—	—
25.3.31	1:7	Ca-Ferrocyanide	1.7×10^{-5}	.80	.80	1.6	1.6	—	—
15.4.31	1:7	$Na_4Fe(CN)_6$	1.9×10^{-5}	.64	.62	1.2	1.3	—	—
2.5.31	1:7	K-Acetate	2.2×10^{-5}	1.7	1.7	3.4	3.5	19.9	10.4

Better agreement was however obtained with another sol with an equiconducting solution of potassium chloride as the upper liquid (vide Table VII). Still better agreement was found by ascertaining the pH of the sol by coagulation with solid potassium chloride and then by dissolving potassium chloride in a potassium hydroxide solution of this pH so that the solution had the same conductivity as that of the sol. It will be seen that this solution gives the best results. The exact composition has thus to be found out by trial and depends on the electrical carriers present in the sol, as given in Table VII.

Generally in measurements of the cataphoretic velocities in this laboratory an agreement between the direct and reverse potential gradient as also in the rate of migration of about 2.5% is considered satisfactory and in view of the uncertainties in visual observation of the position of the boundary further trouble is not taken. It will be seen that it is possible to improve the accuracy, so far as the electrical factors are concerned.

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[1] Slight excess of copper chloride solution was used for the precipitation with potassium ferrocyanide. The specific conductivity of the sol gradually increases with 'age.' This necessitates fresh experiment on each occasion.

[2] See the remarks on the percentage variation in the potential gradient on page 598.

TABLE VII

Upper liquid	Sp. Conductivity of sol and upper liquid	Upward			Downward		
		Pot. gradient		Cataphoretic speed	Pot. gradient		Cataphoretic speed
		Before movement of boundary	After movement of boundary		Before movement of boundary	After movement of boundary	
KCl*	—	.755	.76	44	.741	.743	39
KCl** KOH+	1.4×10^{-5}	.96	.88	38.2	.9	.95	54.4
KCl** KOH+	1.68×10^{-5}	.86	.83	44.3	.88	.91	44.9
KCl**	2.0×10^{-5}	.85	.77	43.7	.89	.91	43.2

* By S. P. Roychoudhury.
** By S. G. Choudhury, the relative amounts of KOH and KCl apparently require to be determined in order to get the most satisfactory boundary conditions.

Aluminum Hydroxide Sol

The following table shows that when electrolytes are present in comparatively large quantities in the intermicellary liquid the ultrafiltrate is quite satisfactory.

TABLE VIII
(S. P. Roychoudhury)

Upper liquid	Sp. conductivity Upper liquid	Sol	Upward		Cataphoretic speed	Downward		Cataphoretic speed
			Pot. gradient			Pot. gradient		
			Before movement of boundary	After movement of boundary		Before movement of boundary	After movement of boundary	
Ultrafiltrate	—	1.25×10^{-3}	.617	.626	34.26	.658	.632	34.65
”	$.31 \times 10^{-3}$	$.22 \times 10^{-3}$	.744	.747	38.1	.742	.696	41
HCl+								
AlCl₃	1.26×10^{-3}	1.24×10^{-3}	.636	.629	31.9	.654	.633	33.9
”	$.7 \times 10^{-3}$	$.68 \times 10^{-3}$	.724	.708	44.5	.691	.68	44.2
”	2.36×10^{-3}	$.23 \times 10^{-3}$	.732	.712	40	.69	.681	43

The ultrafiltrate has however a different sp. conductivity. The approximate constancy of the potential gradient is to be ascribed to the fact that in this case the actual displacement of the boundary (.4–.5 cms.) was very small compared to the effective distance between the side-limbs (3.6 cms.). While an investigation is possible with the method outlined here so as to secure a more satisfactory upper liquid the difference in the case of the ultrafiltrate will only be increased by measuring the potential drop over smaller distances.

Arsenious Sulphide Sol

An equiconducting solution of hydrochloric acid has been found to be satisfactory as the upper liquid.[1] This acid would not have behaved satis-

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[1] Mukherjee: Proc. Roy. Soc., **103A**, 102 (1923); Freundlich and Zeh: Z. physik. Chem., **114**, 84 (1925).

factorily (vide equation 2), as there is an appreciable difference between the mobilities of the negative chloridal particles and that of the chlorine ion, were it not for the fact that free electrolytes (hydrogen sulphide and probably traces of other acids containing sulphur) are present in the sol. The influence, if any, of the chlorine ions on the charge can be experimentally determined. It is possible to produce two boundaries having a marked difference in colour arising out of a mixing of the colloid with the hydrochloric acid. The lower boundary is that of the colloid layer practically unmixed with the electrolyte. The rate of migration of the two boundaries has been followed in detail in several instances by Mr. S. C. Ganguli and it has been observed that the concentration of the chlorine ions does not appear to have an appreciable effect. A more satisfactory boundary should be obtained with hydrogen sulphide solution as upper liquid.

Upper Liquid obtained by freezing the Sol

The supernatant liquid obtained by freezing the particles of the sol has also been used.[1] No investigation has been made as to the suitability of this as the upper liquid for producing a constant potential gradient, a constant rate of migration independent of the direction and an equality in conductivity. Besides the method cannot be generally applicable.

The Microscopic Method

The microscopic method of measuring the cataphoretic speed of colloidal particles has the advantage that in this method the particles move in the same ionic environment. Recently a systematic investigation on this method has been carried out.[2] Even with the improvements suggested by Tuorilla some important difficulties remain to be considered. Firstly, there is an error in calculating the potential gradient. In this method the distance between the electrodes is generally small. For low specific conductivity of sols there is an irregular distribution of the electric field near the electrodes. At higher conductivities the region over which such irregularity spreads becomes smaller. There is thus a greater error in assuming a uniform potential gradient between the electrodes and it varies with the specific conductivity of the sol.

Secondly disturbances arising out of "polarisation" and electrolysis are greater in these small vessels. The potential gradient is thus uncertain.

The third and most important consideration is that the particles stick to the walls forming patches of surface with different properties. Interesting observations are recorded in the literature showing that the wall cannot be *regarded as a uniform interface*. Kruyt and Kadt[3] very recently have observed that particles of colloidal charcoal which behave as positively charged sol showed a negative charge in van der Grinten's cell.[4] But on changing the type

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[1] Pennycuick: J. Chem. Soc., **1930**, 447.

[2] Tuorilla: Kolloid-Z., **44**, 11 (1928).

[3] Kolloidchem. Beihefte, **32**, 249 (1931).

[4] Compt. rend., **178**, 2083 (1924).

of the cell he observed a positive charge in agreement with the other properties of the suspension. The positive charge was confirmed by the moving boundary method. The writer observed (unpublished 1920) that in such experiments as those of Powis on oil emulsions difficulties arise possibly out of the different electro-osmotic velocities near the walls on account of the different charges they carry. It is theoretically impossible to make allowance simultaneously for electro-osmotic currents produced by such irregularly distributed patches in addition to the glass-colloid interface.

Summary

(1) The usual procedures of measuring cataphoretic speeds which avoid measurements of the potential gradient across the boundary are unreliable.

(2) In such measurements there is no evidence (a) that Ohm's law is applicable or (b) that the value of the potential gradient across the boundary is either that which is used in the calculation or that it is at all constant during the movement of the boundary.

(3) The conditions to be fulfilled and the theoretical considerations underlying them have been stated in view of the fact that these are commonly overlooked.

(4) Fresh observations have been given showing in the case of typical colloidal solutions such as those of ferric oxide and copper ferrocyanide, the necessity for ensuring the above conditions of adhering to the writer's method.

(5) The ultrafiltrate, except when the colloid contains considerable quantities of free electrolytes, is unsuitable as an upper liquid for producing the boundary.

(6) Reference has been made to certain important defects of the microscopic method of measuring the cataphoretic speed.

University College of Science and Technology,
Department of Chemistry,
Calcutta,
September 17, 1931.

STUDIES ON SILICIC ACID GELS

I. Measurements on Surface Tension during Setting and the Effect of Temperature on the Time of Set*

BY CHARLES B. HURD AND HENRY A. LETTERON

Introduction

The process of gelation or gel formation offers an interesting field for study to one interested in colloid chemistry. Numerous investigators have studied the formation of gels of hydrated silica or silicic acid gels as they are commonly called. Several theories of the mechanism of formation have been advanced and each has its adherents. The data, however, are not sufficiently complete to permit one to select a theory with any degree of confidence. There is need here, as is usually the case, for more data. We are attempting to secure more data along several lines.

In this paper we shall attempt to present some results on the effect of the temperature on the time of set. By considering the process according to the laws of chemical reactions we arrive at a quantity which in an ordinary chemical reaction would be termed the Heat of Activation.

Historical

We might, of course, study the gelation of pure hydrosols of silica, considering, for the minute, that this system would present the simplest case for study.

A number of investigators have prepared hydrosols of silica. It has been their intention to free the hydrosol as completely as possible from soluble salts, or to produce the hydrosol in such a manner that soluble salts would not be present. Non-salts, if present, have been removed. The interesting fact, for our present study about these hydrosols, is that a number of those who have worked with them report that upon standing these hydrosols set to a gel. Among the workers in this field we may mention several.

Graham[1] obtained the hydrosol by dialysis of the mixture of a solution of water glass and an acid. The same general method has been used by Zsigmondy[2] and more recently by D'yachkovskii.[3]

A rather unusual method was employed by Khalizev,[4] who has dissolved gels of silicic acid in potassium hydroxide solution and then precipitated the potassium with a calculated amount of tartaric acid. This has given him transparent, concentrated sols which may contain 5% silica—always, however, with a small impurity of the tartrate.

* Contribution from the Chemical Laboratory of Union College.
[1] Graham: Pogg. Ann., **114**, 187 (1861).
[2] Zsigmondy: Z. anorg. Chem., **68**, 169 (1910).
[3] D'yachkovskii: Kolloid-Z., **51**, 316 (1930).
[4] Khalizev: J. Russ. Phys. Chem. Soc., **61**, 1233 (1929).

The method of Kröger,[1] who removed the sodium from a water glass solution by electrolysis in a Hildebrand cell using a mercury cathode, appears to be satisfactory. He notes that the setting of these sols to gels occurred very rapidly after the electrolysis had produced a neutral reaction in the solution.

Various methods employing hydrolysis have been used. Ebler and Fellner[2] have subjected the sulfide or chloride of silicon to hydrolysis.[3] The hydrolysis of methyl silicate was utilized by Grimaux[4] and the hydrolysis of ethyl silicate has been used by Inaba.[5]

It would, of course, be possible to study the gelation process, starting with one of these purified hydrosols of silicic acid. In our study we have been unwilling to do this, inasmuch as the preparation of the hydrosol requires a considerable time and involves one or more chemical operations. It would be completely impossible in this way to make any estimate of the time of gelation. We have chosen, therefore, the more complicated study of the system obtained by mixing solutions of sodium silicate and an acid.

There is no scarcity of investigators who have produced silicic acid gel from a solution of a soluble silicate, usually water glass, and an acid. Of the many workers we may mention that Walden[6] indicates that Pott had prepared colloidal silicic acid before 1800.

The work of Graham[7] shows that he was interested in the gelation process. Holmes[8] has described carefully the results obtained by mixing a solution of water glass with a solution of an acid.

In their several papers describing the effects of a number of factors on the setting of silicic acid gels, Prasad and Hattiangadi[9] have in the main used this method.

We have chosen to work with this type of gel-forming mixture because we could then obtain what we call the "time of set."

Experimental

Determination of the "Time of Set."

In studying a chemical reaction, one must have some reliable means of telling when the reaction is complete, or failing this, of determining when the reaction has reached a certain degree of completion. We must admit at this point, that we possess no method by which we can ascertain the exact time at which the gelation process is complete. It appears from our studies that

[1] Kröger: Kolloid-Z., **30**, 16 (1922).

[2] Ebler and Fellner: Ber., **44**, 1915 (1911).

[3] No attempt is being made here to give a complete treatment. The references given in Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, pp. 290 and 304, will provide a good start to anyone interested in a more complete bibliography.

[4] Grimaux: Compt. rend., **98**, 1437 (1884).

[5] Inaba: Sci. Papers Inst. of Phys. and Chem. Research (Japan), **15**, No. 278, p. 1 (1930).

[6] Walden: Kolloid-Z., **9**, 145 (1911).

[7] Graham: Pogg. Ann., **114**, 187 (1861); Phil. Trans., **151**, 183 (1861).

[8] Holmes: J. Phys. Chem., **22**, 510 (1918).

[9] Prasad and Hattiangadi: J. Indian Chem. Soc., **6**, 653, 893, 991 (1929); **7**, 341 (1930).

the process of gelation starts very slowly, sweeps through a maximum of activity, and when the gel is, as we say, "set," the process continues, tapering off into a final hardening or setting process which probably continues for a long time. The formation of the peculiar, lens-shaped bubbles in a silicic acid gel continues for many days, as does the phenomenon of syneresis, indicating an extended time of gelation.

Others have used various tests to determine the time of set. Holmes'[1] test of inverting a test tube to see if the mixture runs out obviously disturbs a gel which has not set, as does Flemming's[2] method of running the mixture through capillary tubes. The optical method of Prasad and Hattiangadi[3] is complicated and, for some of our gels of alkaline reaction which are already opalescent at the start, would be difficult to apply. We have found that a simple and at the same time accurate method consists of inserting a short stirring rod at an angle of about 20° to the vertical into the mixture. If the rod falls over, the gel is considered not set, but if it remains standing, we say that the gel is set.

This gives results in time accurate to two percent, and does not disturb the gel except at the point of insertion of the rod. For 100 cc. beakers we use 3 mm. rods drawn out to a point (fire polished), of a length of about 8 cm. The test is begun when the peculiar opalescence appears which precedes setting.

The Surface Tension of the Solution during Gelation.

The several theories of the mechanism of gelation have in common the idea of a thickening of the structure by an intermeshing of particles or structures in the solution. This has been studied by determining the viscosity but to our knowledge no one has determined the change of surface tension during gelation. Results which we have obtained by a surface tension apparatus appear interesting.

Measurements were made by means of a du Noüy surface tension balance. The sodium silicate was found by analysis to have a composition between $1 Na_2O \cdot 3.0 SiO_2$ and $1 Na_2O \cdot 3.10 SiO_2$. The acetic acid was C. P. glacial acetic acid containing 99.5% CH_3COOH. The watch glass of the du Noüy apparatus was replaced by a larger container so that plenty of fresh surface was available. Readings cease, of course, when the gel has set. A test at this point with the tilted rod method in a separate container would indicate that the gel had set at the point where the ring no longer entered the mixture.

Table I contains the results of this series of tests. The figures are for scale readings on the du Noüy apparatus, multiplication by .728 giving dynes per cm.

Three curves showing scale readings as ordinate against time as abscissae are given in Fig. 1. The three curves have the same shape. The displacement to the right (greater time) occurs as the concentration of acetic acid rises.

[1] Holmes: J. Phys. Chem., **22**, 510 (1918).

[2] Flemming: Z. physik. Chem., **41**, 427 (1902).

[3] Prasad and Hattiangadi: J. Indian Chem. Soc., **6**, 653 (1929).

TABLE I

Variation of surface tension during the process of gelation for three different mixtures

4% Acetic acid			6% Acetic acid			10% Acetic acid		
Time	Temp.	Reading	Time	Temp.	Reading	Time	Temp.	Reading
0.0'	21.0°C	92	0'	25.6°C	76.0	0'	26.0°C	84.0
1.0	23.5	92	10	25.0	74.0	30	24.5	84.0
3.0	23.0	91	20	24.0	74.5	60	23.0	82.0
5.0	22.9	91	30	23.5	75.2	90	22.2	81.5
7.0	22.8	91	40	23.0	81.0	120	21.8	81.0
9.0	22.5	91	50	22.6	79.5	150	21.2	82.5
11.0	22.5	91	60	22.2	83.0	176	21.0	85.0
13.0	22.0	91	70	22.0	82.0	180	"	87.0
15.0	21.8	93	80	22.0	83.0	182	"	90.0
16.0	"	95	90	21.7	86.0	184	"	90.0
17.0	"	96	95	21.7	94.0	186	"	93.0
17.5	"	104	100	21.7	98.0	188	"	98.0
18.0	"	107	105	21.5	120.0	189	"	102.0
18.5	"	108	110	21.5	140.0	190	"	103.0
19.0	"	112	115	21.5	165.0	191	"	103.0
19.5	"	118	116	21.5	180.0	192	"	108.0
20.0	"	124				193	"	110.0
20.5	"	135				194	"	120.0
21.0	"	155				195	"	123.0
21.5	"	155				196	"	135.0
22.0	"	153				197	"	125.0
						198	"	127.0
						199	"	135.0
						200	"	125.0
						201	"	137.0

It will be noted that these runs were carried out without thermostatic control. This control is difficult in the flat dishes used. Later runs where thermostatic control was attempted show results similar to these. The variation of temperature in the results in Table I is therefore not serious.

We cannot, of course, be certain that we have measured a pure surface tension. The effect operates as though it were a surface tension but, at the higher readings at least, we must be dealing with a complicated effect composed of the adhesion to the ring and the tensile strength of the mixture as it gels. From the curves we obtain a picture, however, of the process of gelation, starting slowly, progressing rather uniformly for a considerable time, then sweeping rapidly through a period of great change as shown by the almost vertical portion of the curves. The final portion of the process cannot, of course, be studied in this manner, since the ring of the du Noüy apparatus will not become incorporated into the mass after it has set.

FIG. I
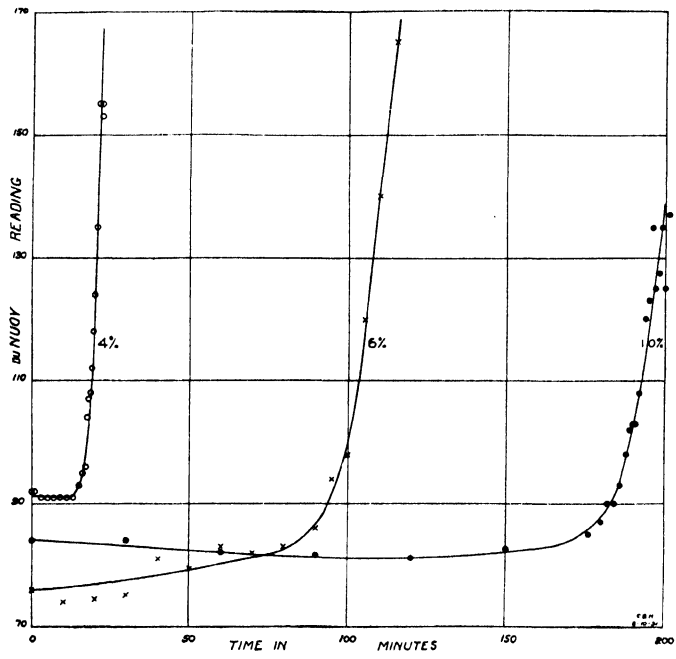
Surface Tension Measurements
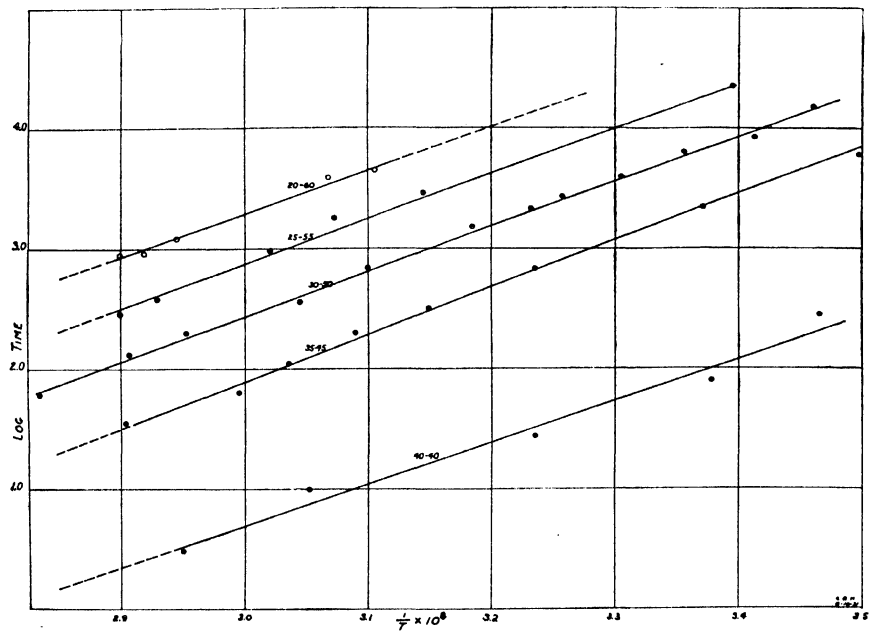
FIG. 2

Effect of Temperature on Time of Set

TABLE II

Variation in time of set with temperature for gels of several differe
concentrations

Temperature Centrigrade	Time of set (secs.)	Log of time of set	Temperature Absolute	Reciprocal absolute temperature $\times 10^3$
Run A 40–40				
15.5°C	283″	2.45179	288.5	3.466
23.0	81	1.90849	296.	3.378
36.0	28	1.44716	309.	3.236
54.5	10	1.00000	327.5	3.053
66.0	3	0.47712	339.	2.950
Run B 35–45				
13.1	5490	3.77379	286.1	3.495
23.6	2200	3.34242	296.6	3.371
36.0	685	2.83569	309.	3.236
44.5	320	2.50515	317.5	3.149
50.5	195	2.29003	323.5	3.090
56.3	122	2.08636	329.3	3.036
65.0	64	1.80618	338.	2.959
71.3	39	1.59106	344.3	2.904
Run C 30–50				
15.5	15000	4.17609	288.8	3.466
20.0	8400	3.92428	293.	3.413
25.0	6360	3.80346	298.	3.356
29.6	3910	3.59218	302.6	3.305
34.0	2645	3.42243	307.	3.257
36.8	2135	3.32940	309.8	3.233
41.0	1507	3.17811	314.	3.185
49.5	690	2.83885	322.5	3.100
55.5	365	2.56229	328.5	3.044
65.5	200	2.30103	338.5	2.953
71.0	132	2.12057	344.	2.907
80.5	60	1.77815	353.	2.833
Run D 25–55				
21.5	22680	4.35564	294.5	3.395
45.0	2910	3.46389	318.	3.145
52.2	1580	3.19866	325.2	3.072
58.0	954	2.97955	331.	3.021
68.2	384	2.58433	341.2	2.930
72.0	289	2.46090	345.	2.899
Run E 20–60				
48.9	4470	3.65031	321.9	3.106
53.0	3830	3.58320	326.	3.067
66.6	1194	3.07700	339.6	2.944
69.5	925	2.96614	342.5	2.919
72.0	780	2.89209	345.	2.599

It is worth noting, at this point, that a curve of this sort may be considered as composed of two effects—the former causing a slow, almost uniform change, and the latter, probably dependent upon the first, progressing rapidly once the effect of the former has reached a certain point. That is what we wish to bring out, that we have here a picture of the first slow process in the setting of a silicic acid gel which must progress to a certain point before the rapid process takes place. We believe the data in the following section will help to reinforce this idea.

Time of Gelation as a Function of Temperature.

We have believed it would prove interesting to consider the process of gelation as analogous to a chemical reaction. With this in view we have measured the time of set for a number of mixtures, although this has been done by several investigators. The time of set was determined by the method described, using a tilted stirring rod. Thermostatic control was carefully observed. The results are given in Table II, and curves showing the logarithm of time as ordinates against reciprocals of absolute temperature are given in Fig. 2.

The designation of the curve such as E 20–60 indicates that 20 cc. of the water glass solution sp. gr. 1.10 was mixed with 60 cc. exactly 1 N acetic acid, for each temperature on the E run. The water glass solution had a gravity of approximately 1.10, but was prepared by dilution and standardized by titration with standard sulfuric acid, using methyl orange. The normality of the sodium silicate solution was adjusted to be equivalent to 1.06 N NaOH. Hence, since the particular sodium silicate used had the composition 1.0 Na_2O, 3.0 SiO_2 this solution was 1.590 molar with respect to SiO_2. This gives us for the composition of the several solutions:

TABLE III

Concentrations of mixtures in Table II in gram mols per liter

	HAc	Na_2O	SiO_2
A—40–40	.50	.265	.795
B—35–45	.563	.232	.696
C—30–50	.626	.199	.596
D—25–55	.688	.165	.496
E—20–60	.75	.133	.398

TABLE IV

Slope of curves of Fig. 2

Curve	Slope $\dfrac{d \log t}{d \frac{1}{T}}$
A—40–40	3488. deg.
B—35–45	3938. deg.
C—30–50	3750. deg.
D—25–55	3750. deg.
E—20–60	3588. deg.
Average	3703. deg.

Curves were drawn to include or approximate the greatest number of points. Straight lines were drawn because they fitted the points better than a smooth curve. It will be noted that the lines appear parallel, although they were not drawn so deliberately.

The slope of the five curves is given in Table IV.

It is interesting to notice that the curves are linear and that their slope is approximately the same, and that the variations from curve E, of lowest silicate concentration, to curve A, of highest, are not regular.

Interpretation of Results

The results obtained suggest immediately that we are dealing with a process which is affected by temperature in much the same manner as are the many ordinary homogeneous chemical reactions which have been subjected to investigation. By our ordinary definition of a homogeneous chemical reaction we include at least the initial reactions which occur here between solutions of sodium silicate and acetic acid.

We do not wish, in this paper, to discuss the several theories for the mechanism of gel-formation, nor to present a theory, but reserve such treatment for a paper which is to follow. However, the data which have been presented offer an opportunity to pave the way for the later theoretical treatment if we permit ourselves to make several assumptions. These assumptions are as follows:

1. That we are dealing with a process which follows the laws of an ordinary chemical reaction so far as its velocity is concerned.

2. That the Arrhenius equation may be applied to our results.

3. That for a given run the time of set measures the time when a certain fixed proportion of the silica, in whatever form, in solution, has reacted.

Concerning this last assumption, it might be pointed out that the ionic reaction between the sodium silicate and the acetic acid is almost certainly a very rapid reaction. The idea that the slow stage of the gelation reaction represents an agglomeration of silicic acid or hydrated silica molecules analogous to a polymerization, may not be so readily accepted. As pointed out under the results on surface tension, we are probably measuring the time for this slow reaction followed by a very rapid process. The time occupied by the latter is necessarily neglected here. The steepness of the final portion of the curves shown by the surface tension data as given in Fig. 1 leads us to hope that this omission will cause no appreciable error here. The same thing has been done, of course, in many studies of the rate of reaction, the results obtained being ascribed to the slow reaction in the series.

We may now utilize our results to calculate the value of the heat quantity Q of Arrhenius' equation. The ordinary expression for the velocity of a chemical reaction

$$dx/dt = k (a-x)^n \qquad (1)$$

where x = the amount changed in time t

a = original concentration

n = order of reaction or the number of molecules of the substance which react

gives when integrated

$$\int_0^x \frac{dx}{(a-x)^n} = \int_0^t k dt \tag{2}$$

$$\frac{1}{n-1}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] = kt \tag{3}$$

In applying expression (1) which is usually used to indicate the result of the interaction of n molecules of the substance A, we are indicating our belief that we are not, in our slow reaction of the series, dealing with a reaction between acetic acid and sodium silicate but are referring to an interaction between like molecules of the same substance. As we have pointed out previously in this article, the ionic reaction between sodium silicate and acetic acid is almost certainly a rapid reaction, as are ionic reactions in general. We then have a picture of the interaction of the results of the first reaction, namely between molecules of silicic acid or hydrated silica. This process would almost certainly be slow as has been shown by the observations of workers on purified hydrosols of silica mentioned in the first part of this article. Our a in equations (1), (2) and (3) we may therefore take to represent the concentration of silica, in whatever form, which results from the ionic reaction of sodium silicate and acetic acid.

It can easily be shown, for any fractional change of a, that the time t'

$$t' = \frac{c'}{ka^{n-1}} \tag{4}$$

where c' = constant depending upon the fraction $\frac{x}{a}$ and on n.

We may now write Arrhenius' equation

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \quad \text{or} \quad \frac{d \ln k}{d\frac{1}{T}} = -\frac{Q}{R} \tag{5}$$

and from (4) $\ln t' = \ln c' - \ln k - (n-1) \ln a$ (6)

If now we maintain a and x/a constant, we may obtain from (5) and (6)

$$\ln t' = + Q/RT - (n-1) \ln a + c'' \tag{7}$$

Since for the various values of a shown in Fig. 2, the slope $\dfrac{d \ln t'}{d\frac{1}{T}}$ is approximately constant, we may obtain the value of Q for curves A to E as

$$Q = R\frac{d \ln t'}{d\frac{1}{T}} = 1.989 \frac{cal}{deg} \times 2.30 \times 3703 \text{ deg} = 16940 \text{ calories}$$
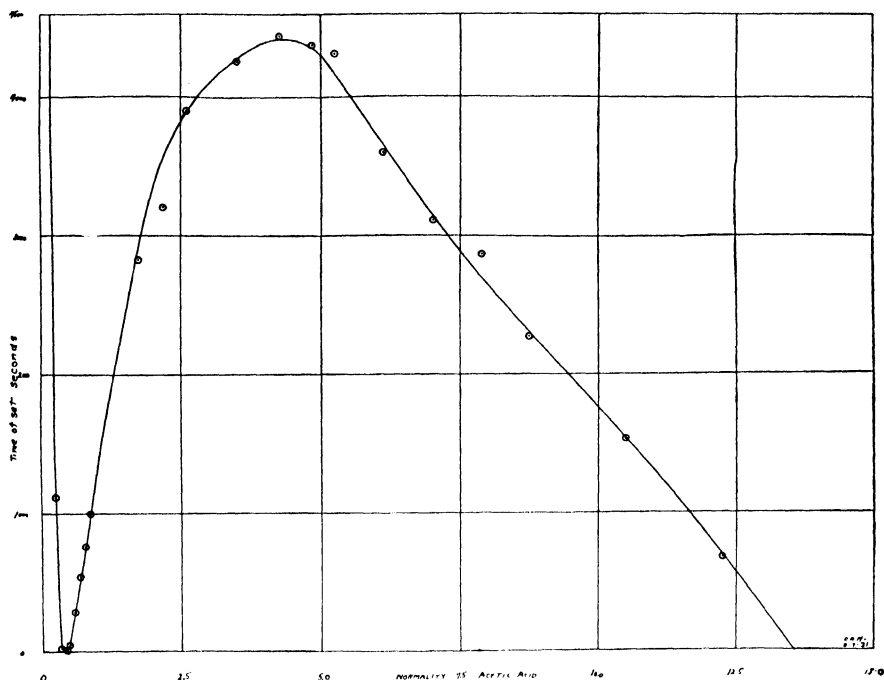
FIG. 3

Effect of Concentration on Time of Set

We thus arrive at a result for Q of 16940 calories. If we were dealing with an ordinary chemical reaction, this would be termed the "heat of activation." It has a value here of the order of the heat of activation for many chemical reactions.

There is a temptation to use equation (6) and the further assumption

4. That in each of the runs A to E the time measured by time of set represents the same fraction of the original concentration, a, converted during the reaction.

If we did assume this, fixing a value for T and knowing the relative values of original concentration of silica in each run, we can obtain for n the following values:

TABLE V

Calculated values of n

Runs	n
A and E	9.67
B and E	6.38
C and E	5.60
D and E	3.70

This variation in n and our knowledge of the large effect on the time of set of the relative amount of acid and sodium silicate, i.e., of the pH of the solution, shows us the last step has been unjustified. If the figures of Table

VI are studied, this last statement will become more apparent. In Table VI are given the results obtained for the time of set as a function of the concentration of acetic acid. The concentration of water glass was maintained constant, corresponding to .53 N NaOH. The concentration of acetic acid was varied, keeping the temperature constant. Two different temperatures were used. The results of the 40° run are plotted in Fig. 3, the 60° run being omitted because it is of the same shape. A concentration of this sodium silicate corresponding to .53 N NaOH of course represents a concentration of .265 g mol Na_2O per liter and .795 g mol SiO_2 per liter. The abscissa of Fig. 3 represents g mols acetic acid per liter and the ordinate time of set in seconds.

A normality of 15.00 is the maximum which can be reached by mixing with concentrated water glass solution if the concentration of the water glass is to be kept constant.

The peculiar hump shaped curve, discovered by Holmes, shown in Fig. 3 for the results of Table VI, shows us that we are almost certainly dealing with a process which is affected catalytically. We cannot therefore utilize

TABLE VI

Time of Set as a function of the concentration of acid
(concentration $Na_2O . 3 SiO_2$ = .265 g mol per liter)

Normality acetic acid	Time 40°C	Time 60°C
.1750		6060 sec.
.2625	1120 sec.	350
.3500	26	10
.4375	5	—
.5250	52	5
.6125	290	—
.7000	540	82
.7875	760	—
.8750	1000	170
1.7500	2820	505
2.1825	3210	—
2.6250	3900	725
3.5000	4260	825
4.2750	4440	870
4.8250	4380	—
5.2500	4320	795
6.1250	3600	740
7.00	3120	645
7.88	2875	525
8.75	2280	415
10.50	1530	238
12.25	675	115
14.00	Too rapid to measure	
15 00	,, ,, ,, ,,	

equation (6) and the data of Fig. 2 to calculate n because no account is taken of the catalytic effect of the H ions (or OH ions) in the solution. We hope soon to be able to present data touching upon this latter phase of the process.

Summary

We have studied the variation of surface tension of a mixture of solutions of sodium silicate and acetic acid during the process of gelation. The reading on a du Noüy apparatus remains almost constant until the mass is about to set, then rises very rapidly. A picture of a slow process followed by a rapid process is suggested.

A satisfactory test for the time of set was devised.

The effect of temperature on the time of set of several mixtures has been determined. By making several assumptions we have been able to calculate a value for Q in Arrhenius' equation, called the "heat of activation" for purely chemical reactions.

Schenectady, N. Y.

THE ADSORPTION OF BINARY VAPOUR MIXTURES
ON SILICA GEL*

BY BASRUR SANJIVA RAO

This paper deals with the adsorption of binary vapour mixtures on silica gel. The object of the investigation was to determine the nature and the extent of the selective adsorption that would take place when a mixture of two vapours was passed over the gel and to elucidate the factors underlying such adsorption.

Earlier Work

Instances of selective adsorption on silica gel have been noticed by several workers. When air containing a mixture of benzene and water vapour was passed over silica gel, E. C. Williams[1] found in one experiment that "in the initial stages, benzene was taken up to the extent of 7.92% of the weight of the gel, but as the passage of the gas was continued, the benzene was gradually displaced by water, until finally no benzene remained in the gel."

Chaney, Ray and St. John,[2] taking note of the fact that silica gel prefers water to toluene and attributing this to difference in wetting action, observe that "differences in wetting action reveal the operation of specific chemical or polar forces, which are not explicable on any mathematical concept as simple as relative capillary diameters."

Patrick and Jones[3] have noted several instances of selective adsorption on silica gel from solutions and ascribe such selective action to the "production of highly concave surfaces of solute which brings about a lowering of the solubility of the solute in the solvent."

Experimental

Selective adsorption on the gel from a binary mixture of vapours was studied by (1) a "static" method and (2) a "dynamic" method.

The Static Method: The apparatus used (Fig. 1) consisted of two tubes L and G containing the liquid and the gel respectively. When the tube L was held with the ground-glass-end opening upwards, it could conveniently be filled with liquid, which would then be in the upper bulb and could be conveyed to its normal position by tilting. G could similarly be filled with the gel. J_1 and J_2 were ground glass joints provided with mercury seals. During the evacuation, the liquid in L was cooled by carbon dioxide refrigerant or by liquid air, while the gel tube was heated to about 320°C by a bath of boiling benzyl benzoate. When the evacuation was complete, the stopcock S was

closed and the apparatus was immersed in a water thermostat at 20°C, so that S was partially submerged under water. A period of 24 to 30 hours was found to be necessary for the attainment of equilibrium. Before removing the apparatus from the thermostat, air was let in. The weight of the liquid used in L, its initial and final composition and the increase in weight of the gel on adsorption, furnished the data necessary for the calculation of selective adsorption.

The *"Dynamic" Method:* In the dynamic method, a circulation pump working in a closed system, conveyed to the gel, vapour from a weighed sample of liquid of known composition. When equilibrium had been attained, the gain in weight of the gel and the change in the composition of the liquid were determined. The data thus obtained enabled the calculation of selective adsorption.

The analysis of the binary mixture of liquids was carried out by means of a Pulfrich refractometer. On an average the composition could be determined with an accuracy of 0.1%.

The pump used for the circulation of the vapour mixture had two pulsating columns of mercury (Fig. 2). It consisted of a U tube A_1R_1 in which the vertical motion of the plunger P caused pulsations of the mercury column in the limb A_1.

FIG. 1
Measurement of Selective Adsorption by the "Static" Method

To the plunger P, which was made of glass and was hollow, was fused a small reservoir R_2 containing mercury. The vertical motion of R_2 caused pulsations of the mercury column in the air chamber A_2. With the aid of the four mercury valves V_1, V_2, V_3, and V_4, and the pulsations produced in the air chambers A_1 and A_2, it was possible to obtain a continuous circulation of air in the bubbler B and the gel tube G. The bubbler and the gel tube were connected to the pump by means of mercury seals. The tube connecting the suction and pressure sides of the pump through a tap S served as a "shunt" in regulating the air passing into the gel-bubbler system. The trap T prevented mercury spray from getting into the bubbler which was similarly provided with a spray trap. Samples for analysis could be removed from the bubbler through a ground glass opening fitted with a stopper.

The vertical motion of the plunger P and the reservoir R_2 was secured by fixing R_2 in a clamp which was raised and lowered by a shaft attached to an eccentric wheel. The eccentric was revolved by a suitably geared motor and made about 50 r.p.m. The air chambers had a diameter of about 1.25 inches and the vertical motion of the mercury column was about 1.75 inches. The pump delivered a fairly constant volume (about 750 cc.) of air per minute and required little attention. It was erected in a suitable air thermostat which was maintained at a temperature of 20 ± 0.1°C.

Adsorption from the Liquid Phase: For purposes of comparison, adsorption from the liquid phase was carried out by dropping a weighed amount (3 to 4 grams) of the activated gel into a small tube containing a known weight of the liquid mixture (volume 4 to 5 cc.). The stoppered tube was then kept for 24 hours in a water thermostat and the change in the composition of the liquid determined.

The Silica Gel: The gel employed in the experiments was in small granules and was a commercial product supplied by the Silica Gel Corporation. Since
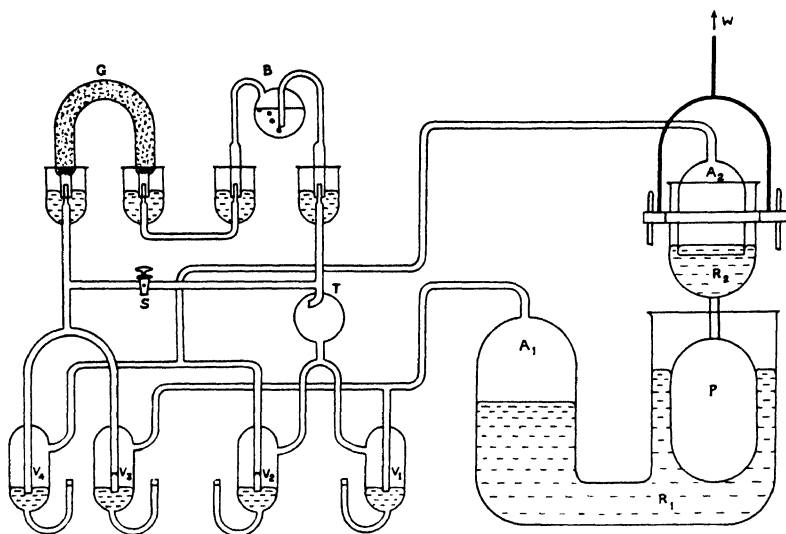
FIG. 2
A Circulation Pump for the Measurement of Selective Adsorption by a Dynamic Method

a sample of this gel, carefully purified by suitable treatment with nitric acid, in no way differed from the original product in its power of adsorbing vapours selectively, purification was deemed to be unnecessary and the commercial product itself was used for the investigations. In the experimental work this gel is referred to as Gel 2. During the activation process, a small portion of this gel accidentally absorbed ammonia and deteriorated in quality. This gel of poor quality is referred to as Gel 1. Another type of gel (Gel 3) used for a part of the work was obtained in the laboratory by Patrick's method. The gels were activated (in a stream of dry air) at 400°C, in a large glass tube heated in an electric furnace.

The chemicals used were specially purified by standard methods of purification and their purity checked by measurement of refractive index.

Calculation of Selective Adsorption: It was found that selective adsorption on the gel from a mixture of two vapours could be conveniently expressed in terms of what might be called "selectivity":

$$\text{selectivity} = s = \frac{x\,(c_g - c_l)}{m \times 100}$$

where x = weight of the liquid held by m grams of the gel

c_g = % composition by weight of the liquid in the gel

c_l = % composition by weight of the bulk liquid (in equilibrium with the gel)

In the experiments wherein the gel was dropped into the liquid and adsorption thus took place from the liquid phase, selectivity was obtained by the relation:

$$s = \frac{w\ (c_i - c_l)}{m \times 100}$$

where w = initial weight of the liquid used in the experiment, c_i the initial and c_l the final composition of this liquid, and m = the weight of the gel. The effect of concentration on the extent of selective adsorption could then be studied by plotting selectivity against concentration of the bulk liquid in equilibrium with the gel.

TABLE I

Adsorption on Silica Gel from Alcohol-Benzene Mixtures at 20°C.

"Dynamic" method		"Static" method		"Liquid phase" method	
% EtOH in bulk liq.	s × 1000 for EtOH	% EtOH bulk liq.	s × 1000 for EtOH	% EtOH bulk liq.	s × 1000 for EtOH
(Gel. 1)				(Gel. 3)	
8.7	29.7			0.06	39.1
26.7	24.1			0.13	97.3
59.0	8.8			1.30	153.3
72.6	4.3			6.40	173.4
				21.62	153.1
				36.18	120.2
				47.11	98.0
				59.89	67.1
				74.01	43.8
(Gel. 2)		(Gel. 2)		(Gel. 2)	
0.18	106.4	29.31	129.1	22.21	150.0
3.72	186.4	48.20	87.2	42.76	114.8
20.09	172.4	62.01	60.3	69.12	58.1
21.61	160.3	78.11	45.2	82.84	25.4
40.02	111.0			97.69	6.2
63.11	66.2				
82.21	31.1				
94.50	10.1				

Water in activated Gel. 1 = 1.4%, Gel. 2 = 2.50%, Gel. 3 = 2.0%.

Results of a few experiments on Gel. 2 (by the dynamic method) given in Table II indicate the remarkable preferential adsorption of alcohol by silica gel from alcohol-benzene mixtures.
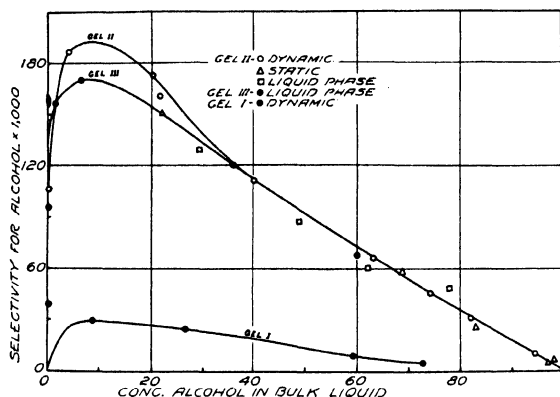
FIG. 3

Selective Adsorption on Silica Gel from Alcohol-Benzene Mixtures

TABLE II

Preferential Adsorption of Alcohol on Silica Gel in Alcohol-Benzene Mixtures

Wt. of gel	Wt. of liq. used	Gain in wt. of gel.	% EtOH in original liq.	% EtOH in residue in bubbler	% EtOH in liq. in gel.
14.91	13.37	5.234	3.30	nil	
14.12	14.94	4.927	6.31	,,	
14.92	10.66	5.297	12.52	,,	
15.37	9.377	5.423	17.63	0.18	30.35
13.80	10.27	4.898	28.78	3.72	56.24
15.38	9.763	5.429	47.25	20.09	68.93

TABLE III

Adsorption on Silica Gel at 20°C from Benzene-Carbon Tetrachloride Mixtures

Dynamic		Static		Liquid phase	
% C_6H_6 in bulk liq.	s × 1000 for C_6H_6	% C_6H_6 in bulk liq.	s × 1000 for C_6H_6	% C_6H_6 in bulk liq.	s × 1000 for C_6H_6
(Gel. 2)		(Gel. 2)		(Gel. 2)	
1.09	29.7	44.82	70.1	15.11	114.2
4.09	32.5	59.78	55.3	30.58	86.6
6.02	116.2	60.49	42.8	73.25	32.8
9.37	126.3			88.00	22.5
20.01	100.1			(Gel. 3)	
29.18	80.8			2.57	33.8
55.20	56.2			5.43	66.9
75.78	35.9			10.17	72.0
94.10	9.1			18.00	71.6
				27.49	70.2
				48.51	60.0
				78.88	26.7

Adsorption from Alcohol-Water, and Acetone-Water Mixtures:—Owing to the comparatively low vapour pressure of water, the experiments by the dynamic method for alcohol-water mixtures were carried out at 40°C. It was found that even then, equilibrium seemed to be established only after 4 to 5 days. The values for selectivity (by the dynamic method) given in Table III show that this method does not give concordant values for water-alcohol mixtures. The static method was also found to be unsatisfactory. Only the "liquid phase" method was therefore employed for acetone-water mixtures.
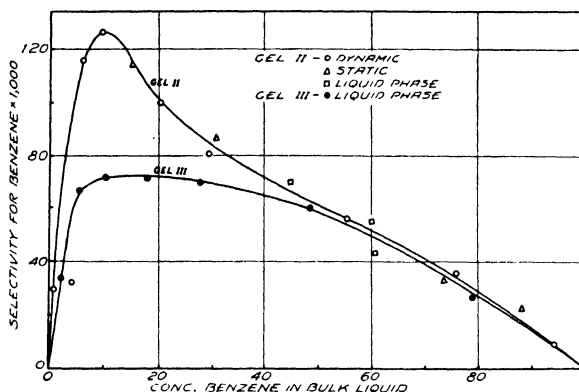
Fig. 4

Selective Adsorption on Silica Gel from Benzene-Carbon Tetrachloride Mixtures

TABLE IV

Adsorption on Silica Gel from Alcohol-Water and Acetone-Water Mixtures.

Alcohol-Water Mixtures				Acetone-Water Mixtures	
Dynamic		Liquid Phase		Liquid Phase	
% EtOH in bulk liq.	s × 1000 for EtOH	% EtOH in bulk liq.	s × 1000 for EtOH	% Acetone in bulk liq.	s × 1000 for Acetone
19.2	+25.4	9.0	+22.9	2.0	+24.2
20.0	+20.2	18.9	+32.2	10.1	+56.0
28.4	+14.3	26.8	+29.0	19.5	+64.3
64.8	−38.8	38.0	+ 8.2	41.4	+58.0
70.3	−65.8	56.0	−40.2	67.1	+20.1
		62.5	−49.9	75.0	0.0
		80.2	−38.2	79.5	−23.1
		88.0	−24.8	85.0	−31.5
				96.0	−16.1

Relative Rates of Adsorption of the Constituent Vapours:—Since the circulation pump gave a fairly uniform circulation of vapour, it was possible by the dynamic method to follow the course of adsorption of each constitu-

ent of a binary vapour mixture. At intervals, the circulation of vapour was stopped, the gel tube was weighed and a weighed sample of liquid from the bubbler analyzed.

Results obtained with four mixtures are given in Table V.

Alcohol-benzene mixture: liquid in the bubbler had 38.8% alcohol.

Benzene-carbon tetrachloride: " " 38.2% benzene.

Water-alcohol (A): " " 65.1% alcohol.

Water-alcohol (B): " " 9.2 % alcohol.

The first two experiments were carried out at 20°C and the last two at 40°C.
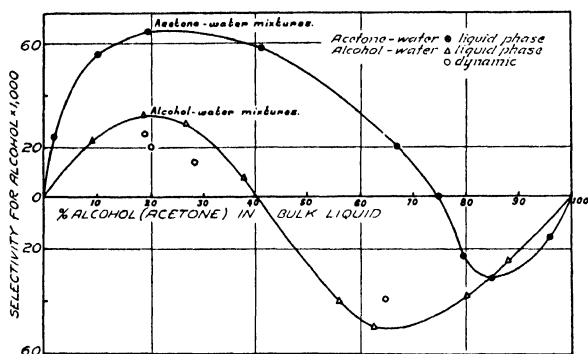
FIG. 5

Selective Adsorption on Silica Gel from Acetone-Water and Alcohol-Water Mixtures

TABLE V

Relative Rates of Adsorption of Constituent Vapours

Alcohol—Benzene Mixture			Benzene-Carbon Tetrachloride		
Duration Expt.	Wt. EtOH adsorbed	Wt. C₆H₆ adsorbed	Duration of expt.	Wt. C₆H₆ adsorbed	Wt. CCl₄ adsorbed
10 mins.	0.419	1.625	10 mins.	0.276	0.756
30 "	0.822	3.937	40 "	0.888	2.026
90 "	2.704	2.531	115 "	2.375	4.089
150 "	3.532	1.775	265 "	2.740	3.528
200 "	3.532	1.775	735 "	2.752	3.522
			795 "	2.752	3.522

Water—Alcohol (A)			Water-Alcohol (B)		
Duration of expt.	Wt. EtOH adsorbed	Wt. water adsorbed	Duration of expt.	Wt. EtOH adsorbed	Wt. water adsorbed
1.5 hrs.	1.595	0.854	0.5 hrs.	0.399	0.741
4.5 "	2.486	1.351	1.5 "	0.654	1.356
10.5 "	3.681	2.018	3.5 "	0.774	2.137
30.0 "	4.728	2.681	24.5 "	1.163	6.302
46.0 "	4.921	2.967	70.5 "	1.178	7.908
90.0 "	4.882	2.967	96.0 "	1.178	7.908

The rate of vapour circulation had been specially reduced in the experiment with benzene-carbon tetrachloride.

Discussion

The experiments on the rate of adsorption of the vapours showed that in the initial stages the composition of the liquid condensed in the gel roughly corresponded with that of the vapour obtained from the liquid in the bubbler. The more volatile constituent however, developed more quickly a "back pressure" which tended to equalise the composition of the liquids in the gel and the bubbler. When the gel selectively adsorbed one of the constituents, the "back pressure" of the constituent preferentially adsorbed was less than what it would have been in the absence of such selective adsorption. Hence, at the equilibrium point the liquid in the gel was richer in the constituent selectively adsorbed.

Experiments in adsorption on silica gel from the four binary mixtures studied showed:

(1) Selective adsorption of alcohol from benzene solutions and selective adsorption of benzene from carbon tetrachloride solutions at all concentrations.

(2) Selective adsorption of alcohol or acetone from dilute aqueous solutions and of water from concentrated mixtures, giving what has been termed the "S" shaped curve for selectivity vs. composition of the bulk liquid.

These results can be explained by considering that the capillaries in silica gel have a water envelope. The following may be adduced in support of the existence of the water envelope:

(1) Heats of wetting of silica gel by several liquids, calculated on the basis of the water envelope, agree well with the experimental values obtained by Patrick and Grimm.[1]

(2) In their attempts to prepare organosols of silicic acid Neuhausen and Patrick[2] found that the water in the gel could not be completely displaced by alcohol, acetone or benzene. It is significant that the organosols finally obtained by them had almost the same percentage of residual water. They concluded that "the residual small percentage of water in silica gel is held with a force that exceeds that exhibited between the atoms of many stable compounds."

(3) Jones[3] concluded from his adsorption experiments that the residual water in activated gel "is apparently occupying a portion of the adsorption space that is unattainable for most other adsorbents."

Silica gel is considered to have a water envelope of the order of 6×10^6 sq. cm. per gram of the gel.[4]

When the gel is dropped into benzene, adsorption finally results in the formation of a benzene-water interface having the same area as the original water envelope. The adsorption of benzene is accompanied by a reduction

[1] J. Am. Chem. Soc., **43**, 2144 (1921).

[2] J. Am. Chem. Soc., **43**, 1844 (1921).

[3] J. Phys. Chem., **29**, 332 (1925).

[4] Patrick and Grimm: loc. cit.; Patrick: J. Phys. Chem., **29**, 220 (1925).

in free surface energy, since thereby a water-air interface with an energy of at least 73 ergs per sq. cm. has been replaced by a benzene-water interface of only 35 ergs per sq. cm. If the gel saturated with benzene is now dropped into water, the benzene is completely replaced, as the adsorption of water leads to the disappearance of the benzene-water interface and a consequential decrease in free surface energy. With a mixture of alcohol and benzene there is a selective adsorption of alcohol as a concentration of alcohol at the water envelope of the gel reduces the free surface energy of the system, alcohol (but not benzene) being miscible with water. In a mixture of benzene and carbon tetrachloride there is a selective adsorption of benzene, as the energy of a benzene-water interface (35 ergs/sq. cm.) is less than that of a carbon tetrachloride-water interface[1] (43.3 ergs/sq. cm.)

Water-alcohol and water-acetone mixtures give with silica gel the "S" shaped curve as there is no marked difference in the selective action of the water envelope on the liquids concerned. Liquid mixtures miscible with water may be expected to give the "S" shaped curve with silica gel. (The author has obtained the S type curve in adsorption experiments on silica gel with binary mixtures of water with acetic acid, pyridine, and piperidine.) Curves of this nature have been explained by Williams[2] as being due to the the simultaneous adsorption of both solvent and solute.

Patrick and Jones[3] ascribe the selective adsorption on silica gel of formic acid, acetic acid and benzene from solutions in kerosene, to the production in silica gel of highly concave surfaces of the solute, causing a lowering of the solubility of the solute in the solvent. The selective adsorption noticed by these authors can be more simply explained by the fact that while a water-kerosene interface has according to Harkins and his co-workers an energy of 57.25 ergs/sq. cm., the two acids used are miscible with water and form practically no interface with the water envelope of the gel. The selective adsorption of benzene can be accounted for by the fact that the energy of the benzene interface with water (35 ergs/sq. cm.) is much less than that of the kerosene-water interface (57.25 ergs/sq. cm.).

The three methods of investigating selective adsorption described in the present communication give fairly concordant values with alcohol-benzene and benzene-carbon tetrachloride mixtures. The "liquid phase" method is the most convenient, while the dynamic method has the merit of enabling a study of the relative rates of adsorption of the vapours. The static method is the least convenient.

Marked differences in selectivity have been noticed with the three gels, working with alcohol-benzene and benzene-carbon tetrachloride mixtures. It may be pointed out that the measurement of selectivity (using suitable mixtures) offers an elegant method of gauging the quality of a sample of silica gel.

[1] Harkins, Brown, and Davies: J. Am. Chem. Soc., **39**, 354 (1917).
[2] Trans. Faraday Soc. **10** (1914).
[3] J. Phys. Chem., **29**, 1 (1925).

Summary

1. A circulation pump for the study of adsorption of vapour mixtures on silica gel by a dynamic method, is described.

2. Results of adsorption experiments on silica gel from benzene-alcohol, benzene-carbon tetrachloride, water-alcohol and water-acetone mixtures are given.

3. The relative rates of adsorption of the constituents of a binary mixture have been studied.

4. An explanation is offered to account for selective adsorption on silica gel.

5. It is suggested that the quality of a sample of silica gel can be conveniently determined by measurement of selective adsorption.

PHOTOLYSIS OF POTASSIUM CUPRIOXALATE

BY HIRA LAL DUBE AND N. R. DHAR

In previous papers[1] from this laboratory we have shown that a solution of potassium cuprioxalate is decomposed in light and the velocity of this photochemical reaction is greatly accelerated by ferric and uranyl salts. No quantitative investigation of this reaction has hitherto been carried out, although the corresponding photolysis of potassium cobaltioxalate,[2] of potassium manganioxalate[3] have received attention. Recently Allmand and Webb[4] have investigated the photolysis of potassium ferrioxalate. The velocity of the photolysis of potassium cuprioxalate is much smaller than those of the decompositions of the above mentioned complex oxalates.

In this paper we have studied the temperature coefficients, quantum yield and light absorption in the photolysis of potassium cuprioxalate in sunlight. The influence of oxygen, carbon dioxide and different amounts of sensitisers on this reaction has also been investigated.

Recrystallised copper sulphate and potassium oxalate were used in preparing the solutions of copper sulphate and potassium oxalate of $N/5$ and normal strength respectively. To obtain potassium cuprioxalate solution, potassium oxalate solution was added to a solution of copper sulphate till the precipitate of cupric oxalate first formed just redissolved and the volume is then made up to 100 c.c. In this way a solution of potassium cuprioxalate of known strength was obtained.

The photolysis of potassium cuprioxalate was studied by exposing the solution directly to sunlight in presence of ferric chloride and uranyl nitrate as sensitisers. The velocity of the reaction was determined by weighing the metallic copper and cuprous oxide formed by the photodecomposition after conversion to CuO. The following are the results obtained:

Time in minutes	Amount of CuO formed in gms.	K_0(Zero-molecular) $= x/t$
60	0.0768	0.00128
120	0.1530	0.00127
180	0.2290	0.00127

The above table shows that the amount of decomposition in a definite time is constant provided the intensity of the light is kept the same. In other words, the photolysis of potassium cuprioxalate is independent of the concentration of the photolyte. This result is identical with that obtained

[1] Dhar: J. Chem. Soc., 111, 694 (1917); Sanyal and Dhar: Z. anorg. Chem., 128, 212 (1923).

[2] Vránĕk: Z. Elektrochemie, 23, 236 (1917).

[3] Ghosh and Kappanna: J. Indian Chem. Soc., 3, 127 (1927).

[4] J. Chem. Soc., 1929, 1518.

by Allmand and Webb in the photolysis of potassium ferrioxalate and by Vránèk in the photolysis of potassium cobaltioxalate. All these reactions appear to be zero molecular.

Temperature Coefficient of the Reaction

The experiments were carried out on different days and as the intensity of sunlight did not remain constant the values of K_o are not the same in the following tables:

No. of expts.	Amount of decomposition in an hour at 27°	K_o at 27°	Amount of decomposition in an hour at 37°	K_o at 37°	Temperature coefficient K_o 37°/K_o 27°
I	0.0424	0.000706	0.0524	0.000873	1.23
2	0.0354	0.000590	0.0432	0.00072	1.22
	37°	37°	47°	47°	K_o 47°/K_o 37°
I	0.0778	0.00129	0.0862	0.00143	1.1
2	0.0686	0.00114	0.0760	0.00126	1.1
3	0.0516	0.00086	0.0570	0.00095	1.1

The quantum yield of this photo decomposition was determined at three temperatures both in the presence and absence of sensitisers. The amount of light absorbed was measured with a Moll thermopile and a sensitive galvanometer. The following are the results obtained:

Temperature	Sensitiser	Quantum yield
27°		0.49
37°	None	0.73
47°		0.66
27°		0.54
37°	0.000237 N ferric chloride	0.88
47°		0.81
27°		0.53
37°	M/20000	0.77
47°	uranium nitrate	0.72

These results indicate that the quantum yield is slightly less than unity. The quantum yield appreciably increases in presence of the sensitiser.

Effect of Oxygen and Carbon Dioxide on the Reaction

To test the influence of oxygen and carbon dioxide on the reaction two pairs of solutions were taken in beakers. The first pair was exposed to sunlight and through one of them oxygen was passed. Similarly through one

of the other pair carbon dioxide was passed. The experiments were repeated on several days and following results were obtained:

Time of exposure	Decomposition without a current of air CuO obtained	Decomposition in a current of air CuO obtained
3 hours	0.1398	0.0722
3 hours	0.1594	0.0636 in a current of CO$_2$
3 hours	0.1506	0.1492
3 hours	0.1656	0.1470
3 hours	0.1227	0.0936
3 hours	0.1360	0.1155

It is observed that the velocity of the reaction is retarded in presence of both oxygen and carbon dioxide. The retardation in the case of carbon dioxide is, however, much less than in the case of oxygen. The behaviour of oxygen as an inhibitor is not uncommon. The photolysis of Eder's solution, of ferric oxalate and of ferric salts of other organic acids is stated to be retarded by oxygen. Recently Allmand and Webb have observed that the photodecomposition of potassium ferrioxalate is also inhibited by air. This inhibition is probably due to the oxidation of ferrous salt formed by the insolation of ferric chloride used as sensitiser. Ferric chloride is first reduced to the ferrous condition photochemically and this then acts as a sensitiser. When, however, oxygen is present this process is retarded due to the oxidation of the ferrous salt. Similar must be the case when uranium salt is used as a sensitiser. The primary action of this salt appears to be its reduction to the uranous condition, which acts as sensitiser and the process is inhibited by oxygen. This conclusion appears to be supported by the experiments of Boll and Henri[1] on the photoreaction between uranyl nitrate and oxalic acid.

Influence of an Excess of Potassium Oxalate

A slight excess of potassium oxalate solution has practically no effect on the velocity of the reaction, while a large excess is found to accelerate the photodecomposition of potassium cuprioxalate. In the case of potassium ferrioxalate and potassium cobaltioxalate, it is found that the reactions are retarded by an excess of potassium oxalate, while it has no effect in the case of potassium manganioxalate.

The following results obtained by us indicate an acceleration of the photodecomposition of potassium cuprioxalate by the addition of large quantities of potassium oxalate.

Time of exposure	Excess of N.K$_2$C$_2$O$_4$	Amount decomposed as CuO (1)	(2)	(3)	(4)
1 hour	0 c.c.	0.0654 gms.	0.0662 gms.	0.0582 gms.	0.0620 gms.
,,	10 c.cs.	0.0756	0.0698	0.0708	0.0780
,,	20 c.cs.	0.0804	0.0854	0.0802	—

[1] Compt. rend., 158, 32 (1914).

The effect of varying the concentration of the sensitiser on the rate of decomposition of potassium cuprioxalate has also been investigated and the following results have been obtained:

(1) N/42.19 ferric chloride solution has been used as a sensitiser.

Time of exposure	Ferric chloride in c.cs.	Amount of decompo-sition in gms.
3 hours	0.0 c.c	0.0126
,,	0.2	0.0142
,,	0.5	0.0178
,,	1.0	0.0220
,,	2.0	0.0342
,,	3.0	0.0416
,,	4.0	0.0392

(2) M/2 Uranium nitrate solution used as sensitiser.

Time of exposure	Uranium nitrate added in c.cs.	Amount of decompo-sition in gms.
3 hours	0 c.c	0.0134
,,	2	0.0180
,,	3	0.0192
,,	4	0.0198
,,	5	0.0180

From the foregoing tables it is apparent that the velocity of the reaction goes on increasing as the amount of sensitiser is increased but there is a limit after which further increase in the concentration of the sensitiser brings about a fall in the velocity of the reaction. The increase in the velocity of the reaction by adding the sensitiser is mainly due to the increase in the absorption in the ultraviolet portion of the spectrum. In the visible region of the spectrum no increase in absorption is observed as will be clear from the following results obtained in the measurement of the extinction coefficient of the solutions using Nutting's spectro-photometer.

(1) Ferric chloride used as a sensitiser.

Region	Amount of sensitiser in c.c. added to $K_2Cu(C_2O_4)_2$	Extinction coefficient
6700 Å		0.87
6300 Å	1 c.c of 0.023 N $FeCl_3$	0.55
6000 Å		0.35

There is no absorption in the other regions of visible spectrum.

6700 Å		0.87
6300 Å	2 c.cs of 0.023 N $FeCl_3$	0.55
6000 Å		0.35

The extinction coefficients of potassium cuprioxalate solutions without any sensitiser were practically the same in these regions. There is no absorption in other regions of the visible spectrum.

(2) Uranium nitrate used as a sensitiser.

Region	Amount of sensitiser added to $K_2Cu(C_2O_4)_2$	Extinction coefficient
6700 Å		0.88
6300 Å	0.4 c.c of $M/200$ uranium nitrate	0.59
6000 Å		0.38

No absorption in other wavelengths.

6700 Å		0.88
6300 Å	1 c.c of $M/200$ uranium nitrate	0.59
6000 Å		0.38

Some photographs of the absorption spectra of potassium cuprioxalate solutions with and without any sensitiser were taken using a quartz spectograph and copper arc as a source of light. The spectra showed a complete absorption in the ultraviolet region in all the three cases. It thus appears that ultraviolet light is mainly responsible for this photodecomposition. Moreover, no photodecomposition was observed when solutions of potassium cuprioxalate were exposed to the total light from a 1000 watt gas filled tungsten filament lamp for five hours.

Discussion

The photodecomposition of potassium cuprioxalate can probably be represented by the equation:

$$K_2Cu(C_2O_4)_2 \rightarrow K_2C_2O_4 + CuC_2O_4$$

No cupric oxalate is, however, formed actually but an admixture of copper and cuprous oxide is obtained in the photodecomposition of potassium cuprioxalate. It, therefore, appears that somehow the cupric oxalate formed is instantaneously decomposed. Our experimental results, however, show, that cupric oxalate, either by itself or in the presence of a sensitiser, is not decomposed by light. Cupric oxalate was exposed as a freshly precipitated solid as it scarcely dissolves in water. It is just possible that the cupric oxalate, which is formed by the decomposition of potassium cuprioxalate is in an activated state at the time of its formation and that it is instantaneously decomposed by the absorption of light energy into copper, cuprous oxide and carbon dioxide. It is observed that the reaction in light is extremely slow in the absence of a sensitiser like ferric chloride or uranyl nitrate. The primary action of light, therefore appears to be the activation of the sensitiser molecule.

$$\text{Sensitiser} + h\nu \rightarrow (\text{Sensitiser}),' \text{ activated}$$
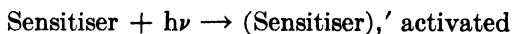
The energy is transmitted to potassium cuprioxalate which is then activated

$$K_2Cu(C_2O_4)_2 + (\text{Sensitiser})' \rightarrow K_2\,Cu(C_2O_4)_2' + \text{Sensitiser}$$
$$\text{(activated)}$$
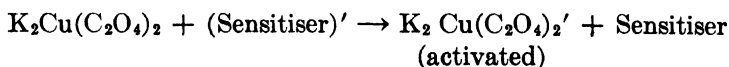
The sensitiser which is probably the ferrous salt is now again free to absorb more light energy and transmit it to potassium cuprioxalate.

In the case of potassium ferrioxalate decomposition, Allmand and Webb assume the activation of ferrioxalate ion which on collision with an inactive molecule gives rise to ferrous oxalate ion, the maximum quantum yield being thus two. In our case this cannot be the mechanism for we have observed that the quantum yield for the photolysis of potassium cuprioxalate is less than unity. We assume, therefore, that an activated molecule of potassium cuprioxalate on collision with an inactive molecule of the same give rise to molecules of activated cuprioxalate. Thus:—

$$K_2Cu(C_2O_4)'_2 + K_2Cu(C_2O_4)_2 \rightarrow 2K_2C_2O_4 + 2\ CuC_2O_4'\ \text{(activated)}$$
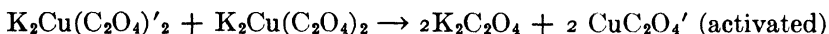
We have observed that freshly precipitated cupric oxalate is not decomposed by light even in the presence of a sensitiser; so it must be an activated molecule of cupric oxalate, which takes a further quantum of light through the medium of the sensitiser and gets itself decomposed, the energy being given out as heat. Moreover it will be seen that the energy of the activated cupric oxalate molecule is half of the amount absorbed by the molecule of potassium cuprioxalate; hence absorption of more energy is essential for its photodecomposition.

$$Cu(C_2O_4)' + \text{Sensitiser}\ h\nu \rightarrow CuC_2O_4 + \text{Sensitiser}$$
$$\text{(activated)}$$

This then decomposes as

$$CuC_2O''_4 \quad \rightarrow \quad Cu + 2\ CO_2 \qquad \text{(i)}$$
$$CuC_2O''_4 \quad \rightarrow \quad CuO + CO + CO_2 \ \text{(ii)}$$

and $\qquad Cu + CuO \ \rightarrow \ Cu_2O$
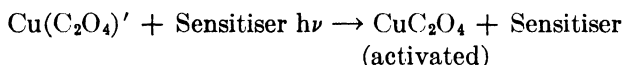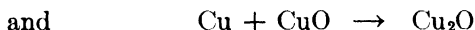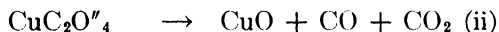
Thus we finally get copper, cuprous and cupric oxide as decomposition products. It also explains why the photoequivalent law of Einstein is not exactly applicable, less than a molecule being decomposed for every quantum of light energy absorbed. Hence it will be clear that from the mechanism of decomposition proposed here, the quantum yield should be 0.5. The observed values approach the expected result.

Summary

1. The kinetics, temperature coefficient, and quantum yield of the photolysis of potassium cuprioxalate solutions sensitised by ferric and uranium salts have been studied in sunlight. It is observed that the order of the reaction is zero.

2. Einstein's law of photo-chemical equivalence is not exactly applicable. Nearly 0.5 molecule decomposes per quantum of light energy absorbed; the temperature coefficient of the reaction, $K_{037}/K_{027} = 1.22$ and $K_{047}/K_{037} = 1.1$.

3. The presence of either oxygen or carbon dioxide retards the reaction. The inhibiting effect of oxygen appears to be due to its oxidising the reduced sensitiser; the reduction of the sensitiser appears to be the primary process before it acts as a sensitiser. Although a small excess of potassium oxalate has no effect on the photolysis of the reaction, a large excess is found to accelerate the decomposition.

4. There is a limit to the increase in the velocity of the reaction by increasing the concentration of the sensitiser after which the velocity falls. The sensitising action is due to the increase in absorption in the ultraviolet portion of the spectrum. The reaction appears to be due mainly to ultraviolet radiations.

5. The primary process in the photodecomposition is the activation of the potassium cuprioxalate molecule, which on collision with an inactive molecule gives rise to activated cupric oxalate molecule, which by the absorption of further quantum decomposes finally into copper, cuprous and cupric oxide and carbon dioxide. This mechanism explains the experimental observations.

Our best thanks are due to Mr. W. V. Bhagwat for his help in the experiments and in the writing of the paper.

Chemistry Department,
University of Allahabad,
Allahabad, India,
March 19, 1931.

CERTAIN CORRELATIONS BETWEEN THE CONSTITUTION OF DYES AND THEIR COLOR INTENSITY*

BY A. R. PETERSON[1] AND W. C. HOLMES[2]

Investigations during the past fifty years have thrown much light upon the manner and degree in which constitutional variations of many types influence the hue of dyes, but their effect upon intensity of color appears to have been ignored almost completely. This may probably be attributed, primarily, to the fact that color may only be investigated advantageously in terms of light absorption and that the spectroscope, which is adequate only for the determination of the spectral locations of the maxima of absorption bands, has been widely available for many years, whereas the spectrophotometer, which is indispensable for the investigation of absorption intensities, is of much more recent development and still finds only restricted use. Very little data have been published which are suitable to serve as a basis for the comparison of the relative color intensities of different dyes. This paper records the results obtained in a preliminary study of color intensity with solutions of a comprehensive selection of dyes.

The criterion of color intensity selected was the absorption of dye solutions at the approximate absorption maxima of the dyes. It is admitted that color intensity can be defined completely only on the basis of absorption measurements covering the complete visible spectrum. Hue, also, can be defined completely only on a similar basis, but it is customary to consider maxima locations alone in studying the influence of constitution upon hue, and that course has proved adequate in general practice. It seems probable, similarly, that absorptions at the maxima will afford an essentially reliable criterion of color intensity.

It is obvious that data on color intensities may be reduced to two common bases for comparison. Intensity may be expressed as *specific absorption*, on the basis of a given absolute concentration of solute, or as *molecular absorption*, on the basis of a given molar concentration of solute. For the purposes of this investigation, specific absorption is defined as the absorption in terms of the Bunsen extinction coefficient (E) of a one centimeter layer of a solution containing one one-hundred-thousandth of a gram of actual† dye per cubic centimeter of solution, measured at the approximate absorption maximum of

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† Dyes ordinarily contain appreciable proportions of moisture, inorganic salts or other impurities. The term "actual dye," as employed herein, implies 100% dye. In other words, the true dye content of all samples employed was determined and appropriate allowance made for all impurities.

the solution. Molecular absorption is defined as the similar value, determined similarly, with a solution containing one one-hundred-millionth of a mole of actual dye per cc. of solution.

It will be seen that specific absorptions afford a basis for comparing color intensities upon what may be referred to as the practical basis. Equal specific absorptions imply that the same concentrations of different dyes have equal intensities. Molecular absorptions afford a comparison upon the molecular basis. Molecular absorptions indicate directly how the color intensity of the molecule is influenced by variations in constitution.

It will be seen, further, that the molecular absorption of a given dye should be independent of the salt-forming radical with which it is associated, whereas its specific absorption should be different for each dye salt. The chloride, bromide, iodide, acetate and benzoate of rosanilin, for example, should have a common molecular absorption but different specific absorptions. These relations were found valid in this investigation when the solvents employed were of a suitable character. The various rosanilin salts enumerated had the same molecular absorptions within limits of experimental error in aqueous solutions. They also had a common molecular absorption in alcohol. In chloroform, however, the molecular absorptions of these salts were found to vary. Certain of the chloroform solutions were obviously colloidal, as shown by their instability.

Both specific and molecular absorptions were found to vary with the solvent employed. The absorption of a given concentration of rosanilin chloride, for example, is greater in chloroform than in water, greater in ethyl alcohol than in chloroform, and greater in methyl than in ethyl alcohol. Similar variations in intensity of absorption are generally encountered with all dyes in different solvents. In respect to unconformity to general rule, they resemble the displacements in spectral locations of absorption bands of dyes with change in solvent. It appears probable that intensity is conditioned upon constitutional factors[3] and may be attributed to rearrangements of residual affinities within the dye molecule resulting from the interplay of affinities of solute and solvent.

Apart from the variations in color intensity which appear normal with change in solvent, the investigator may often observe secondary effects arising from other causes. Changes in solvents may modify tautomeric equilibria between dye forms, or influence the relative state of molecular aggregation, and in all such instances the absorption of the dye undergoes corresponding modification.

In view of such considerations, it was considered inadvisable to rely entirely upon any one solvent in this investigation. The solvents selected were water and 94% alcohol. Both are excellent solvents for dyes, in general, and very dilute solutions of dyes, such as were employed for the measurements, are seldom decidedly colloidal in either solvent. Alcohol is unquestionably somewhat more satisfactory for the purpose in view, in general, than is water, since many of the dyes investigated do not exist completely in a single tau-

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[3] Holmes: J. Am. Chem. Soc., **46**, 2118 (1924).

TABLE I

Specific and Molecular Absorptions of Dyes in Water and in Alcohol

Dye	Colour Index No.	Water Max. (mμ)	Water Spec. Abs.	Water Mol. Abs.	94% Alcohol Max. (mμ)	94% Alcohol Spec. Abs.	94% Alcohol Mol. Abs.
Croceine Orange	26	490	.46	.16	490	.37	.13
Orange G	27	495	.49	.22	490	.44	.20
Ponceau 2G	28	490	.42	.19	490	.38	.17
Chromotrope 2R	29	510	.66	.31	520	.64	.30
Fast Crimson GR	31	530	.57	.29	540	.57	.29
Azogrenadine S	54	510	.53	.27	505	.47	.24
Azogrenadine L	55	508	.45	.23	505	.37	.19
Fast Fuchsine 6B	56	530	.63	.33	535	.63	.33
Fast Crimson 6BL	57	530	.62	.35	535	.65	.37
Janus Green	133	615	1.00	.51	620	1.04	.53
Niagara Blue 2B	406	585	.76	.71	585	.78	.73
Azo Blue	463	555	.71	.51	560	.78	.57
Niagara Blue 3B	477	590	.72	.69	600	.73	.70
Diamine Blue 3R	490	540	.49	.36	560	.77	.57
Pontamine Blue AX	502	565	.51	.39	595	.66	.50
Niagara Sky Blue	520	610	.63	.62	600	.67	.66
Benzo Blue R	566	545	.53	.47	565	.81	.71
Benzo Indigo Blue	568	570	.63	.58	590	1.07	.98
Benzo Black Blue G	578	565	.49	.51	573	.54	.57
Benzo Blue Black 5G	579	585	.40	.44	595	.48	.52
Malachite Green	657	626	2.36	.88	623	2.63	.98
Brilliant Green	662	625	2.05	.99	628	2.49	1.20
Guinea Green B	666	618	1.20	.83	628	1.63	1.13
Fast Acid Green B	667	635	1.45	1.05	643	1.50	1.09
Light Green SFY	670	633	1.16	.91	633	.79	.63
Brilliant Blue (Na salt)	671	630	1.70	1.35	625	1.76	1.39
Fast Green FCF[4]		628	1.50	1.21	620	1.55	1.25
Xylene Blue VS	672	640	2.26	1.28	630	2.36	1.33
Brilliant Blue A	673	638	1.55	1.07	630	1.71	1.18
Chrome Green pdr.	674	620	1.26	.59	620	1.58	.47
Para rosanilin (Chloride)	676	540	2.50	.81	548	3.09	1.00
Rosanilin[5] (Chloride)		543	2.32	.78	551	2.91	.98
Crystal Violet	681	590	2.35	.96	590	2.67	1.09
Ethyl Violet	682	594	2.01	.99	594	2.52	1.24
Benzyl Violet	683	590	1.75	.85	590	2.27	1.10
Victoria Blue 4R	690	590	1.44	.75	590	1.78	1.04
Acid Rosaniline[6]		545	.89	.52	553	1.43	.84

[4] The p-hydroxy analog of Brilliant Blue.
[5] The chloride of triamino-diphenytolyl-carbinol anhydride.
[6] The disodium salt of the trisulphonic acid of rosaniline.

TABLE I (Continued)

Specific and Molecular Absorptions of Dyes in Water and in Alcohol

Dye	Colour Index No.	Water			94% Alcohol		
		Max. (mμ)	Spec. Abs.	Mol. Abs.	Max. (mμ)	Spec. Abs.	Mol. Abs.
Patent Blue VN	712	638	1.96	1.13	630	2.13	1.23
Patent Blue A	714	638	1.52	1.07	630	1.72	1.21
Night Blue	731	595	1.11	.64	610	1.68	.97
Pyronine G	739	545	2.74	.83	545	2.67	.81
Pyronine B	741	550	3.15	1.13	555	3.48	1.25
Rhodamine B	749	555	2.03	.97	545	1.96	.94
Fluoresceine	766	490	.55	.22	488	1.08	.44
Dibromo fluoresceine[7]		508	1.20	.64	515	1.51	.81
Tetrabromo fluoresceine[8]		510	.90	.62	523	.96	.66
Eosine	768	516	1.36	.94	528	1.46	1.01
Ethyl Eosine	770	522	1.50	1.07	535	1.75	1.25
Eosine B	771	518	1.39	.87	525	1.49	.93
Erythrosine	772	528	1.12	.99	535	1.18	1.04
Phloxine B	778	538	1.21	1.00	548	1.37	1.14
Rose Bengal B	779	548	.96	.98	558	1.13	1.15
Neutral Red[9]	825	535	1.25	.36	538	1.77	.51
Phenosafranine	840	520	1.30	.42	535	1.79	.58
Safranine	841	520	1.12	.40	530	1.51	.54
Iris Violet	847	586	1.31	.57	579	1.56	.68
Cresyl Blue[10]		625	1.07	.31	622	1.35	.39
Cresyl Violet[11]		593	.97	.33	618	1.27	.41
Naphthylene Blue R	909	568	1.61	.50	570	1.61	.50
Fast Cotton Blue B	910	570	1.01	.45	575	1.06	.47
Nile Blue A	913	635	1.42	.52	630	1.99	.73
Thionine	920	601	2.31	.61	604	3.53	.93
Methylene Blue	922	663	2.35	.75	658	3.07	.98
Tetra ethyl thionine		670	2.37	.89	660	2.76	1.04
Indigotine	1180	610	.45	.21	610	.47	.22

tomeric form in the latter solvent[12] even under the conditions of examination. While the data obtained in aqueous solutions may be more reliable in specific instances, it is believed that those obtained in alcohol are more trustworthy.

The general method of examination was the following: Dye samples were selected, as far as was possible, with normal absorption ratios,[13] indicative of

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[7] Substituted in the resorcinol residues.
[8] Substituted in the phthalic anhydride residue.
[9] Examined with the addition of 1% acetic acid.
[10] Amino-pheno-dimethylamino-tolazoxine chloride.
[11] Amino-naphtho-dimethylamino tolazoxine chloride.
[12] Holmes: Ind. Eng. Chem., 16, 35 (1924).
[13] Holmes and Peterson: Stain Technology, 5, 65 (1930).

substantial freedom from color impurities. Many of the samples taken were recrystallized. Their dye contents were determined by titration with titanous chloride or other appropriate means. Stock solutions of .1% strength were prepared in water and 5-cc. aliquots were diluted to 500 cc. with water and with 95% alcohol, respectively. The extinction coefficients of these solutions were then measured immediately at their respective maxima with a Bausch and Lomb spectrophotometer of the most recent type, and the specific and molecular absorptions of the dyes (as previously defined) calculated, where (E) equals the Bunsen extinction coefficient with a one-centimeter layer of solution, (M) equals the weight in grams of one mole of the dye and (W) equals the weight in grams of actual dye in one gram of crude dye,

the specific absorption $= E/W$

and the molecular absorption $= \dfrac{E \times M}{W \times 1000}$

All solutions were preserved for a considerable period and re-examined periodically for evidence of colloidal characteristics. Certain dyes which gave decidedly colloidal solutions were rejected. A few dyes were also rejected because of uncertainty respecting their constitution or dye content.

The data obtained in these determinations are recorded in Table I. Specific and molecular absorptions are given in water and in 94% alcohol, together with the wave lengths at which the dyes were examined. The identity of the individual dyes is indicated by the Colour Index number recorded in the following column, or by footnotes when necessary.

Although the recorded data could be employed for the quantitative evaluation of dyes with the spectrophotometer they were not obtained under optimum conditions for that purpose and are not recommended therefor. It is believed that they are reasonably reliable and satisfactory, however, to serve as an index of relative color intensity.

Specific absorption values range between .42 and 3.15 in water and between .37 and 3.53 in alcohol; molecular absorptions between .16 and 1.35 in water and between .13 and 1.39 in alcohol.

The majority of dyes examined may be grouped in three general categories, azo derivatives, triphenylmethane derivatives (including phthaleins) and quinonimide derivatives. Average values for the dyes of these three categories are given in the following summary:

TABLE II

Average Specific and Molecular Absorptions of Three Principal Dye Groups

Dye Group	No. of Samples	Specific Absorption Water	Specific Absorption 94% Alc.	Molecular Absorption Water	Molecular Absorption 94% Alc.
Azo	20	.59	.64	.41	.46
Triphenylmethane	30	1.55	1.80	.89	1.02
Quinonimide	12	1.51	1.95	.51	.65

In each group color intensity is greater in alcohol than in water.

On the basis of specific comparison there is comparatively little difference in the average relative intensity of triphenylmethane and quinonimide dyes, whereas both groups of dyes are much more intensely colored than are azo dyes. On the molecular basis of comparison, triphenylmethane derivatives are decidedly more intensely colored in both alcohol and water than are quinonimide derivatives, and the latter are more intensely colored than are azo derivatives.

A similar tabulation of average values is given in Table III for a more detailed classification of dyes.

TABLE III

Average Specific and Molecular Absorptions of Sub Groups of Dyes

Group	No. of Samples	Specific Absorption Water	94% Alc.	Molecular Absorption Water	94% Alc.
Monazo	10	.58	.56	.29	.28
Disazo	6	.64	.73	.55	.62
Trisazo	4	.51	.72	.50	.70
Triphenylmethane diamino	12	1.65	1.82	1.02	1.09
Triphenylmethane triamino	8	1.80	2.29	.79	1.03
Pyronine	2	2.95	3.08	.98	1.03
Phthalein	10	1.22	1.39	.83	.94
Azine	4	1.25	1.66	.44	.58
Oxazine	5	1.22	1.44	.42	.50
Thiazine	3	2.34	3.12	.75	.98
Indigotine	1	.45	.47	.21	.22

Considered on the molecular basis of comparison, with particular regard given to the data obtained in alcoholic solution, these values warrant the additional conclusions that there is comparatively little difference in color intensity between the pyronines and both di- and triamino triphenylmethane derivatives, and that phthaleins and thiazines are but little less intense. The thiazines are much more intensely colored than azines or oxazines. Disazo dyes are decidedly more strongly colored than monazo dyes, but the effect of further azo linkages is slight. On the specific basis of comparison, pyronines and thiazines are extremely intense in color. Further generalizations on the influence of general dye type upon intensity of color appear inadvisable without more data, particularly since the criterion employed is probably somewhat less reliable as between dyes of different types than between dyes of the same general type.

The range in minor constitutional variation in the individual dyes available for examination was very considerable, and in numerous instances the data obtained will have clear significance only in the light of further investigation with other related dyes. Considerable direct evidence of the influence

of minor constitutional variation on color intensity, however, may be found in the tabulated values. This will be considered, briefly, from the view-point of molecular absorption.

The influence of sulfonation is shown to be very variable. The sulfonation of rosanilin reduces its color intensity considerably. The sulfonation of the benzidine nucleus, in components of polyazo dyes, also decreases color strength materially. On the other hand, sulfonation usually increases color intensity in monazo dyes (cf. 26, 27 and 28). With diamino triphenylmethane derivatives, the disulfo substitution in the non-aminated nucleus increases color intensity (cf. 662 and 672). In this same nucleus it would appear that sulfonation in the ortho position increases color intensity, whereas sulfonation in the para position decreases it (cf. 666, 670 and 671).

The influence of the hydroxyl group appears similarly variable. The introduction of a hydroxyl group in the 8 naphthalene position with Azo-grenadine S increases color intensity decidedly (cf. 54 and 56), but the intro-duction of a hydroxyl group in the non-aminated nucleus of diamino triphenyl-methane derivatives decreases color strength (cf. Fast Green FCF and 671, 712 and 672).

With azo dyes the introduction of an acetylamino group has a general effect similar to that of a hydroxyl group (cf. 29 and 31, 56 and 57). With Ponceau 2G, Chromotrope 2R and Fast Crimson GR, its introduction in the para benzene position increases color intensity; with Azogrenadine S its introduction in the 8 naphthalene position increases color strength even more decidedly (cf. 28 and 55, 29 and 56, 31 and 57, 54 and 57).

With polyazo dyes, the replacement of Neville and Winther's acid in the end positions by H acid increases color intensity (cf. 477 and 502). As an inner component of polyazo dyes, benzidine gives greater color strength than tolidine, and tolidine greater intensity than dianisidine (cf. 406, 477 and 520, 463 and 502). Ethoxybenzidine is approximately equivalent to tolidine and gives greater color intensity than dianisidine (cf. 463 and 490, 490 and 502). Tolidine gives much greater color intensity than benzidine-3,3'-disulfonic acid (cf. 566 and 578, 568 and 579).

In the diamino triphenylmethane class, the double diethyl substitution gives more intensely colored products than the corresponding ethylbenzyl substitution (cf. 672 and 673, 712 and 714).

In the fluoresceine molecule, the identity of the halogen substituent is relatively unimportant, but the degree of halogenation has considerable influence on color intensity (cf. dibromo-fluoresceine with eosine). The general locality of halogenation is particularly important. Tetrabromofluoresceine, in which the bromination occurs in the phthalic anhydride residue of the molecule, is much less strongly colored than is eosine, in which a corresponding degree of bromination occurs in the resorcine residues of the molecule.

The influence of alkyl substitution in triphenylmethane and quinonimide derivatives appears generally consistent. Alkyl substitution within the ben-zene nuclei appears to decrease color intensity slightly (cf. P-rosaniline and

rosaniline, phenosafranine and safranine). On the other hand corresponding substitution at amino groups increases color strength decidedly (cf. 681 and 676, 782 and 676, 847 and 840, 922 and 920 and tetraethyl thionine and thionine). Ethylamino substitution increases color intensity in an appreciably greater degree than does corresponding methylamino substitution (cf. 662 and 657, 682 and 681, 741 and 739, and tetraethyl thionine and methylene blue).

The recorded data afford other evidence, of a direct or indirect character, on the effects of other minor constitutional variations. Only a few of the more interesting instances will be cited. It is noteworthy that the diazotization of safranine and its conversion into an azo dye (Janus Green) is not accompanied by any appreciable increase in molecular absorption. The loss in color intensity resulting from the introduction of a carboxylic acid group into the Malachite Green molecule (with the formation of Chrome Green powder) is somewhat extreme. A similar extreme decrease in color intensity (unrecorded) is observed when Crystal Violet is converted into Methyl Green. The gain in color intensity with the ethylation of eosine also appears somewhat surprising, and suggests the possibility that the explanation of the observed effect may be found in the influence of the esterification in stabilizing the dye in quinoid form.

Further conclusions appear unwarranted at this time. It seems evident that both major and minor constitutional variations in dyes have, in general, a definite effect upon color intensity. Although the influence of some types of substitution appears to be somewhat constant, in nature if not in degree, it seems evident that substitution in general may exert very diverse effects upon color intensity, depending upon the general dye structure involved, upon the precise position in which the substitution occurs and upon the degree and nature of previous substitution within the parent molecule. It is obvious that molecular absorption is influenced by many factors and that its adequate explanation will necessitate extended investigation.

It may be pointed out, finally, that, in general, substitution affects specific absorption and molecular absorption in decidedly different ways. Whereas the molecular absorption of any given dye is usually increased by substitutions which increase its molecular weight, it is seldom that color intensity increases in full proportion with molecular weight. The general effect of substitution is to decrease color intensity on the specific basis.

Summary

(1) The extinction coefficients of dye solutions at their absorption maxima were adopted as criteria of color intensity.

(2) The specific and molecular absorptions of sixty-five dyes were determined in water and in alcohol.

(3) On the molecular basis of comparison, triphenylmethane derivative and pyronines are the most intensely colored of the dye groups investigated,

with phthalines and thiazines but slightly less intense. Disazo and trisazo dyes, oxazines and azines are less intensely colored, while monazo dyes and indigotine have relatively low intensity.

(4) On the specific basis of comparison, pyronines and thiazines have exceptional color intensity.

(5) Within any given dye group molecular absorption is usually increased by substitutions which increase molecular weight or molecular complexity, whereas specific absorption is commonly decreased thereby.

(6) Although certain regularities are noted, the effects of substitutions, in general, appear variable, depending upon the general dye structure involved, upon the precise position in which substitution occurs, and upon the nature and degree of previous substitution within the dye molecule. Molecular absorption is clearly influenced by a variety of different factors.

COMPOSITION OF PRECIPITATED COPPER SULFIDE

BY I. M. KOLTHOFF AND E. A. PEARSON[1]

The composition of the precipitate obtained by passing hydrogen sulfide into a solution of a cupric salt has been a matter of dispute for a long time. Thomsen[2] claimed that the precipitate obtained with hydrogen sulfide from neutral solutions of copper sulfate was not pure cupric sulfide, for sulfur could be extracted from the precipitate with sodium or ammonium sulfide yielding a solution of polysulfide. Ditte,[3] however, believed that pure CuS is formed and that sulfides decompose the copper sulfide.[4] By extracting fresh and aged precipitates of copper sulfide with carbon disulfide in an atmosphere of carbon dioxide, Brauner[5] found increasing amounts of sulfur removed from the sulfides; he also assumed a decomposition of CuS. Coppock,[6] also Antony and Lucchesi,[7] claimed that the fresh precipitate is pure CuS, as the ratio of copper and sulfur found in the compound was 1:1. It is evident that such an analysis does not prove that cupric copper and sulfide are present in the precipitate in the same ratio. Rossing[8] applied Heumann's[9] method to the problem and extracted the copper sulfide with silver nitrate:

$$Cu_2S + 4\ AgNO_3 \rightarrow Ag_2S + 2\ Ag + 2\ Cu(NO_3)_2 \quad (1)$$

$$CuS + 2\ AgNO_3 \rightarrow Ag_2S + Cu(NO_3)_2 \quad (2)$$
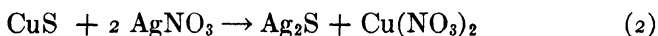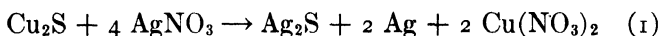
From the amount of silver found in the precipitate, he concluded that copper sulfide obtained from hydrogen sulfide and copper sulfate solution was pure CuS. However, as Feigl[10] has pointed out, he forgot to take into account the possibility of free sulfur being present (Brauner,[5] Gluud.[11])

The sulfur would react with silver ion, and, therefore, in analyzing a mixture of CuS and equimolecular quantities of Cu_2S and S, one always would find a result as represented by equation (2). By an improved method of analysis, E. Posnjak, Allen and Merwin[12] arrived at the same conclusion. They made use of the fact that ferric nitrate oxidizes metallic silver quanti-

[1] From a thesis submitted by E. A. Pearson to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Thomsen: Ber., 11, 2043 (1878); J. prakt. Chem., 19, 4 (1879).

[3] Ditte: Ann. Chim. Phys. (8), 12, 229 (1907).

[4] See also, Abel: Z. anorg. Chem., 26, 411 (1901).

[5] Brauner: Chem. News, 74, 99 (1896).

[6] Coppock: Chem. News, 73, 272 (1896); 76, 231 (1897).

[7] Antony and Lucchesi: Gazz., 19, 545 (1890).

[8] Rossing: Z. anorg. Chem., 25, 413 (1900).

[9] Heumann: Ber., 7, 1680 (1874).

[10] Feigl: Z. anal. Chem., 72, 32 (1927).

[11] Gluud: Ber., 55, 1760 (1922).

[12] Posnjak, Allen and Merwin: Z. anorg. Chem., 94, 131 (1916), comp. also for the analysis of a mixture of CuS and Cu_2S, Posnjak: J. Am. Chem. Soc., 36, 2475 (1914).

tatively (comp. equation 1) whereas it does not affect silver sulfide. Before digesting the copper sulfide with silver nitrate they did not extract sulfur from the former. Still sulfur might be present, especially in aged precipitates. Gluud[11] showed that fresh and aged copper sulfide (obtained in alkaline medium) behave differently toward potassium cyanide solution. The aged, but not the fresh precipitate, yields thiocyanate, thus indicating the presence of free sulfur in the former. Gluud believes that CuS is very unstable and can be obtained only in exceptional cases, ordinary copper sulfide is probably

$$\begin{matrix} Cu \\ \diagdown \\ \diagup \\ Cu \end{matrix} S = S.$$ Probably the CuS first formed decomposes in the following

way, as suggested by Feigl:[10]

$$2\ CuS \rightarrow \begin{matrix} Cu \\ \diagdown \\ \diagup \\ Cu \end{matrix} S = S \rightarrow Cu_2S + S$$
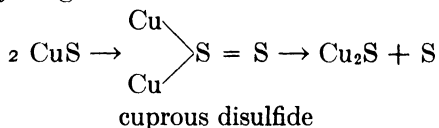
<div align="center">cuprous disulfide</div>

The cuprous disulfide composition is in agreement with results of Pickering[13] and the work of Lowry and Gilbert.[14] Jordis and Schweizer[15] in agreement with other workers found that copper sulfide obtained by precipitation always contains some free sulfur. Its quantity varied with the temperature to which the sulfide had been exposed, being greatest in the precipitate obtained from hot solutions. The precipitates extracted for a long time with various solvents gave up amounts of sulfur which increased in amount with increasing boiling point of the solvent used. Young and Neal's[16] work appears to support strongly the interpretation of the spontaneous decomposition of cupric sulfide on aging.

Feigl[10] concludes that there is at present no satisfactory method of determining the composition of copper sulfide. He developed a new method of analysis and concluded that copper sulfide freshly precipitated from acid solution at room temperature contained about 1.5% cuprous sulfide, whereas precipitates which were three days old (from acid, neutral and alkaline medium) contained 6.5 to 7.5% cuprous sulfide.

Summarizing this literature review, it seems fairly certain that fresh precipitates of copper sulfide prepared at room temperature have the empirical formula, CuS, and that on aging they gradually decompose into cuprous sulfide and sulfur.

In the interpretation of the inducing effect of copper sulfide on the precipitation of zinc sulfide,[17] it was desirable to know something more definite about the composition of the sulfide formed by treating copper sulfate with hydrogen sulfide under different conditions. Therefore, a short study has been made, the results of which are described below.

[13] Pickering: J. Chem. Soc., **39**, 401 (1881).
[14] Lowry and Gilbert: Nature, **123**, 85 (1929).
[15] Jordis and Schweizer: Z. anorg. Chem., **23**, 577 (1910).
[16] Young and Neal: J. Phys. Chem., **21**, 14 (1917).
[17] Comp. previous paper J. Phys. Chem., **36**, 549 (1932).

Experimental

In analyzing the copper sulfide a modified Posnjak[12] method was followed. The original procedure as proposed by Posnjak has certain objections and even the modified method is not ideal for the following reasons:

a. In extracting sulfur from the precipitate the latter may already undergo a slight decomposition. Moreover, it seems doubtful whether all sulfur can be extracted from the precipitate.

b. Ferric salts react slowly with silver sulfide, especially if the latter is finely divided. It was found in this work that the longer time of extraction of the mixture of silver and silver sulfide with the ferric iron solution, the more silver appeared in the filtrate. This error was reduced in our experiments by working under uniform conditions and running blanks with silver sulfide under similar conditions.

The modified Posnjak method for the analysis of copper sulfide which was used in the following work was as follows: 25 cc. 0.05 molar copper sulfate solution were precipitated with hydrogen sulfide at room and at higher temperatures from acid and neutral media. The fresh or aged precipitates were filtered and quickly washed free from sulfate and hydrogen sulfide with distilled water and then with methyl or ethyl alcohol. The filter papers containing the precipitates were placed in fat extractors (Soxhlet) extracted with carbon disulfide (or ether) for about ten to fifteen hours, and transferred into beakers containing 50 cc. of 5% silver nitrate solution in each case. The covered beaker was placed on a steam bath and digestion with occasional stirring was carried out for three hours in order to complete the transformacion (see equations 1 and 2). The precipitate was then filtered off, washed free of silver ion, transferred into a beaker and extracted twice at 70° with 25 cc. portions of 6% ferric nitrate. Duration of each extraction was two minutes. The solutions were filtered hot and the filtrate, after washing the precipitate, strongly acidified with nitric acid, evaporated to about 100 cc. and titrated with standard thiocyanate.

The calculation of the percentage cuprous sulfide originally present in the copper sulfide is based on the equations (1) and

$$Ag + Fe^{+++} \rightarrow Ag^+ + Fe^{++} \quad (3)$$
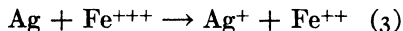
Notes: 1. As silver sulfide reacts slowly with ferric nitrate blanks were run with 25 cc. 0.1 N silver nitrate. After precipitation at room or boiling temperature with hydrogen sulfide, the washed precipitates were treated with ferric nitrate as described in the above procedure. As an average, a correction of 3% (± 0.5%) had to be subtracted in the actual experiments from the percentage cuprous sulfide found to account for the inter-action between silver sulfide and ferric nitrate under the conditions mentioned.

2. In most cases it was shown that after digestion of the copper sulfide with silver nitrate no copper was present in the precipitate, showing the completeness of reactions (1) and (2).

3. The sulfur extracted after evaporation of the solvent was weighed in all cases. The weights are not reported here as the sulfur often was contaminated with a thin film of copper sulfide. It was noticed that aged precipitates

and those prepared at high temperature yielded more sulfur in the carbon disulfide than those obtained at room temperature and immediately extracted. In the latter case the amount of sulfur found was negligibly small. Its presence might be attributed to a slight air oxidation of copper sulfide. In washing the precipitates with alcohol before the extraction, those prepared at high temperature or precipitated at room temperature and aged gave off some sulfur. Incidentally, it may be mentioned that freshly precipitated copper sulfide at room temperature has a black or brownish-black appearance and is easy to filter. On aging it assumes the same greenish appearance as a precipitate formed at higher temperature, moreover, it becomes slimy and hard to filter.

Some results are given in Table I. The aged precipitates were allowed to stand for the time indicated in the presence of an excess of hydrogen sulfide in the absence of air.

TABLE I

Decomposition of Copper Sulfide precipitated by Hydrogen Sulfide

Temp. of precipitation	Acidity of solution at start of precipitation	Age of ppt. before extraction	% Cu_2S in copper sulfide
room	neutral	fresh	0.3
,,	0.36 N H_2SO_4	,,	0.3
,,	,, ,,	7 days	2.0
,,	,, ,,	,,	2.1
boiling	neutral	fresh	5.0
,,	0.36 N H_2SO_4	,,	5.3
,,	,, ,,	,,	4.7
,,	,, ,,	9 days	7.1
,,	,, ,,	,,	7.7

In agreement with Feigl it was found that freshly precipitated copper sulfide at room temperature virtually does not contain cuprous sulfide. On aging at room temperature under hydrogen sulfide cuprous sulfide is slowly formed. If formed from boiling solution copper sulfide contains about 5% cuprous sulfide. On aging of this precipitate at room temperature under hydrogen sulfide, the cuprous sulfide content increases slowly. Whether the transformation of cupric sulfide to cuprous sulfide and sulfur is complete after a long time of standing has not been investigated.

Summary

Copper sulfide precipitated at room temperature from cupric sulfate solution with hydrogen sulfide is practically pure cupric sulfide. After aging for seven days under hydrogen sulfide it contains about 2% cuprous sulfide. Precipitates from boiling solutions contain about 5% cuprous sulfide, this amount slightly increasing on aging at room temperature.

School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota.

THE RADIATION HYPOTHESIS OF CHEMICAL REACTIONS AND THE CONCEPT OF THRESHOLD WAVELENGTH

BY G. GOPALA RAO AND N. R. DHAR

The rapid increase of velocity of a thermal reaction with temperature is one of the outstanding difficulties in the theoretical treatment of chemical dynamics on the basis that there are active and inactive molecules in any system at a given temperature, and increase in the velocity of a reaction with temperature is due mainly to the increase in the proportion of active molecules. Arrhenius[1] first derived an equation showing the relation between temperature and reaction velocity. This relation can be written as

$$\frac{d \log k}{dT} = \frac{E}{RT^2}$$

Subsequently, Marcelin[2] and Rice[3] arrived at a similar relation on the basis of statistical mechanics. According to them E is the energy of activation, that is the energy necessary to convert 1 mole of normal molecules into the active state. It becomes obvious, therefore, that the theory of activation and the idea of critical energy increment are necessary to account for the influence of temperature on chemical reactions.

Arrhenius, Marcelin and Rice have not however suggested any mechanism by which molecules become activated. How does a molecule receive the critical energy increment before it reacts? These are fundamental questions, and an answer to this was provided in the general radiation theory of chemical change, put forward originally in an obscure form by Trautz[4] and considerably developed by W. C. McLewis[5] and Perrin.[6] Briefly stated, the hypothesis is, that the increase in internal energy, which a molecule must receive before it is capable of reacting, (that is the critical energy increment E) is communicated to it by infrared radiant energy present in the system by virtue of its temperature; the addition of energy being made in terms of quanta of the absorbable type. The velocity of a reaction is therefore determined by the intensity of that radiation and depends only on the temperature in the measure that the intensity depends upon it. In the activation of molecules a narrow band of infrared frequencies was assumed to be operative. If the molecules are activated by more or less monochromatic radiation, then the frequency for the effective radiation can be calculated from the relation

$$E = N h\nu$$

[1] Arrhenius: Z. physik. Chem., **4**, 226 (1889).
[2] Marcelin: Compt. rend., **157**, 1419 (1913); **158**, 116, 407 (1914); Ann. Phys., (9) **3**, 120 (1915).
[3] Rice: Brit. Ass. Rep., 387 (1915).
[4] Trautz: Z. wiss. Phot., **4**, 160 (1906); Z. physik. Chem., **76**, 129 (1911).
[5] W. C. McLewis: J. Chem. Soc., **109**, 796 (1916); **111**, 387, 457, 1087 (1917); Phil. Mag., **39**, 26 (1920).
[6] Perrin: Ann. Phys., (9) **11**, 5 (1919).

E is the energy of activation, the value of which can be obtained from the temperature coefficient of the reaction, N is Avogadro's number and ν is Planck's constant. Thus, the radiation hypothesis represents an extension of Einstein's law of photochemical equivalence.

There are three consequences of the radiation hypothesis which should serve as a test for its validity. (1) Firstly the frequency calculated from E must correspond to a wavelength in the observed absorption band. (2) The reaction must be greatly accelerated by light of the calculated wavelength, and (3) thirdly the total amount of energy corresponding to this wavelength in the dark must be sufficient to activate the requisite number of molecules so as to account for the dark reaction. Now let us consider the evidence on these three heads. Lewis and coworkers have shown that in a large number of cases the observed and calculated frequencies do agree. Ethylsulphonium bromide has been shown by von Halban to decompose into ethyl bromide and diethyl sulphide in a unimolecular manner in various solvents. Taylor and Lewis have shown that in this case the calculated and observed absorption lines show a remarkable agreement in the case of eight solvents studied. Similar coincidence was obtained in the case of the inversion of sucrose (Moran and Taylor[1]) in the conversion of γ-hydroxybutyric acid into the lactone (Garret and Taylor[2]) and in the hydrolysis of acetamide (Meehan[2]). A further case is the transformation of fused maleic acid into fumaric acid; of course, there are some cases of disagreement also (Cf. Langmuir[3]).

Furthermore, Lewis on the basis of certain calculations made with the help of the radiation theory, predicted in 1918 that ozone should be decomposed by visible light. Griffith and Shutt[4] showed that ozone is decomposed by light of wavelength larger than 6700 Å near the red end of the spectrum. On the other hand, Lindemann has pointed out that the inversion of sucrose (which has a temperature coefficient of 4.13 corresponding to wavelength 10580 Å) must be greatly accelerated by sunlight which contains a large proportion of this wavelength; and reported that such indeed is not the case. Dhar,[5] however, has shown that the reaction is greatly accelerated by sunlight. Furthermore, Daniels and Johnston, working with nitrogen pentoxide decomposition, and Framegot, studying the reduction of ceric salts by acetaldehyde in acid solution, have reported that insolation with appropriate wavelength does not lead to increased reaction velocity. There appears to be some contradiction, therefore, on the second point.

The hypothesis as originally put forward by Lewis, fails more completely when we consider the third deduction:—it has been shown by Langmuir (loc. cit.) that the radiation theory cannot account quantitatively for the observed rate of dissociation of phosphine. Similar calculations made by Christiansen and Kramers[6] in the case of nitrogen pentoxide decomposition

[1] J. Am. Chem. Soc., **44**, 2886 (1921).
[2] "A System of Physical Chemistry," **3**, 226, (1924).
[3] Langmuir: J. Am. Chem. Soc., **42**, 2090 (1920).
[4] Griffith and Shutt: J. Chem. Soc., **119**, 1948 (1921).
[5] N. R. Dhar: Z. anorg. allgem. Chem., **119**, 177 (1921).
[6] Christiansen and Kramers: Z. physik. Chem., **104**, 451 (1923).

show that, if activation by monochromatic radiation is assumed, it is not possible to account for the observed rate of decomposition. It appears that if activation by a more or less continuous band of frequencies of some considerable width is assumed then there would be sufficient absorption in unit time to account for the number of molecules transformed.

Nevertheless there is a considerable body of opinion in favour of some form of radiation hypothesis. The acceleration of many reactions by light shows that there is nothing improbable in principle about the supposition that molecules are activated by ordinary temperature radiation. Without some form
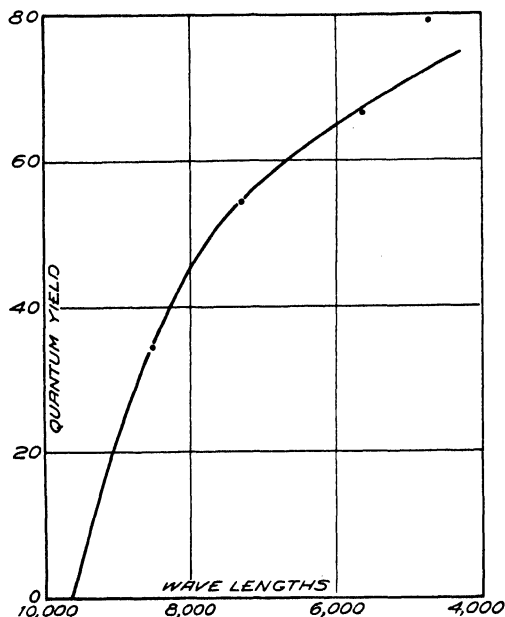
FIG. 1
Potassium Oxalate and Bromine

of radiation hypothesis, it appears difficult to account for the occurrence of unimolecular gaseous reactions e.g. decomposition of nitrogen pentoxide [the alternate activation mechanisms put forward by Lindemann (assuming a time lag between activation by collision and chemical change) and by Christiansen and Kramers (reaction chain mechanism) have been shown to be inadequate. Cf. Hinshelwood[1]].

In view of this one of us[2] has put forward the conception that the wavelength calculated from the critical energy increment may be regarded as the threshold limit. No acceleration of the chemical change is possible with radiations of wavelengths longer than the threshold limit, while wavelengths shorter than the threshold wavelength will accelerate the chemical change, provided they are absorbed. The main difference between this conception

[1] Hinshelwood: "Kinetics of Chemical Changes in Gaseous Systems," 126-129 (1926).

[2] Dhar: J. Phys. Chem., 33, 850 (1929); J. Indian Chem. Soc., 6, 451 (1929).

and the Perrin-Lewis radiation hypothesis is that according to the latter view the wavelength calculated from the temperature coefficient of the reaction should bring about the maximum speed of the reaction in question, whilst according to the conception now put forward, the threshold frequency is the minimum frequency necessary for carrying out the reaction. Now we have devised a new method of arriving at this threshold wavelength from altogether independent lines. A number of photochemical reactions have been studied in this laboratory in radiations of different wavelengths. It is found in general that the quantum yield of any one reaction, that is the number of molecules reacting per quantum of light absorbed, decreases with increase in the wavelength of the light.
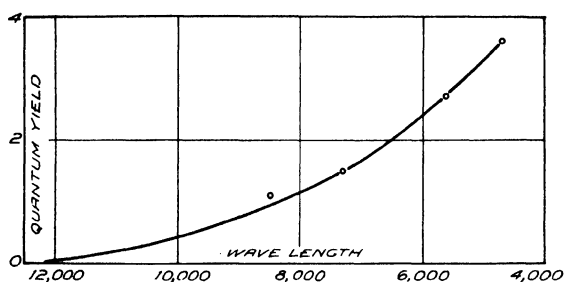
FIG. 2

Citric Acid and Chromic Acid

The following table illustrates this point of view:—

Reaction	Quantum yield in wavelength 4725 Å	Quantum yield in wavelength 5650 Å	Quantum yield in wavelength 7304 Å	Quantum yield in wavelength 8500 Å
Citric acid and chromic acid (24°)	3.6	2.7	1.5	1.1
Pot. oxalate and bromine (20°)	7.9 × 10	6.66 × 10	5.44 × 10	3.43 × 10
Inversion of cane sugar 35°	8.41 × 10²	7.32 × 10²	4.43 × 10²	2.82 × 10²
Sodium cobaltinitrite (20°)	3.75	2.24	1.1	0.92
Sodium cobaltinitrite (40°)		9.60	6.0	3.90

If now we plot the quantum yields against the wavelengths and extrapolate the curve to zero quantum yield, we can get the wavelength with which there should be no acceleration of the chemical change, that is the threshold limit referred to above. Now all these reactions take place in the dark also, so that the threshold limit can be obtained from the temperature coefficient of the dark reaction. The close agreement between the values of the threshold wavelength obtained by the two methods lends great support to our conception.
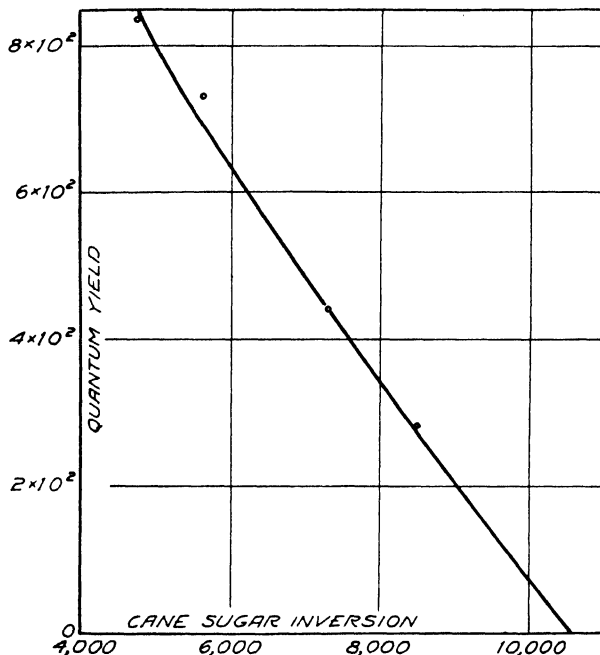
FIG. 3

Reaction	Threshold wavelength calculated from the temperature coefficient of the dark reaction	Threshold wavelength obtained from the graph
Citric acid and chromic acid	12000 Å	12,200 Å
Potassium oxalate and bromine	9400 Å	9,600 Å
Sodium cobaltinitrite	13000 Å	13,500 Å
Inversion of cane sugar	10580 Å	10,600 Å

See Graphs 1 to 3.

Summary

1.   Some sort of radiation hypothesis appears to be necessary. It is well known that the hypothesis as originally put forward by Lewis and Perrin is untenable. A modified view of the radiation hypothesis is put forward. According to this new conception, the wavelength calculated from the temperature coefficient of the dark reaction, represents the threshold limit. Wavelengths longer than this will have no action, whereas wavelengths shorter than this limiting value will accelerate the reaction, provided they are absorbed.

2.   A second method of obtaining this threshold wavelength is described. Many photochemical reactions have been studied in our laboratory in different wavelengths. It is found that the quantum yield in any reaction generally decreases with increasing wavelength. We have plotted the wavelengths against the quantum yield; and by extrapolation of the curve to zero quantum yield, the threshold wavelength is obtained. This can also be obtained from a knowledge of the temperature coefficient of the dark reaction.

3.   The close agreement between the values of the threshold wavelength obtained by the two methods lends support to the new conception of the radiation hypothesis put forward.

Chemical Laboratory,
University of Allahabad,
Allahabad, India,
March 19, 1931.

THE SOLUTION OF OXYGEN IN SILVER[*]

BY J. H. SIMONS

The high solubility of oxygen in molten silver and its subsequent release upon solidification is a well-known phenomenon. Quantitative determinations of the amount of the gas dissolved at different temperatures and pressures have been made by Sieverts and Hagenacker[1] with a confirming determination at one temperature by Donnan and Shaw.[2] The crystalline metal has also been shown to have a high solubility for the gas, and Steacie and Johnson[3] have made determinations of this over a wide temperature and pressure range. That the metal retains some of the oxygen that it dissolves when molten upon solidification has been shown by a number of investigators,[4] but the quantity so retained is reported differently by the different investigators, indicating that this quantity depends upon the experimental conditions.

The ability of silver to dissolve oxygen is specific for this gas for hydrogen is retained only slightly[1] and nitrogen and the inert gases hardly at all.

The various hypotheses that have been advanced to account for this phenomenon are discussed in some detail by Mellor.[5] There are three possible means of accounting for the solution. The first of these is that oxygen is dissolved as O_2; but this is extremely improbable, as the amount dissolved in either the crystalline metal as shown by Steacie and Johnson,[3] or in the liquid as shown by Sieverts and Hagenacker,[1] is proportional to the square root of the pressure. Either of the other two hypotheses would explain this relationship. One of these is that the oxygen dissolved is in the atomic state, a mechanism similar to the one frequently proposed for the solution of hydrogen in platinum or palladium. The other is that the substance dissolved is silver oxide Ag_2O; but that at the temperatures at which oxygen is apparently dissolved the silver oxide is unstable and owes its existence to the fact that it is dissolved in silver, and the solution has reduced its activity.

Experiments so far conducted do not distinguish between these two hypotheses. In addition to the change of solubility with pressure Donnan and Shaw[2] have noted that the freezing point of silver heated in air is lower than that heated in vacuum or inert atmosphere by an amount which agrees with the calculated lowering calculated from the quantity of either silver

[*] Contribution from the Chemical Laboratory of Northwestern University.

[1] Sieverts and Hagenacker: Z. physik. Chem., **68**, 115 (1909).

[2] Donnan and Shaw: J. Soc. Chem. Ind., **29**, 987 (1910).

[3] Steacie and Johnson: Proc. Roy. Soc., **112A**, 542 (1926).

[4] Dumas: Compt. rend., **86**, 68 (1878); Brauner: Bull. Acad. Belg., **18**, 81 (1889); Richards and Wells: Z. anorg. Chem., **46**, 79 (1906).

[5] Mellor: "A Comprehensive Treatise on Inorganic and Physical Chemistry," **3**, 342 (1923).

oxide or atomic oxygen dissolved. They have, however, favored the silver oxide hypothesis, reasoning by analogy from the solution of copper oxide in copper and the lack of solution of oxygen in gold.

It was thought that if molten silver were cooled rapidly enough, it might retain some of its oxygen content at room temperature in the form in which it existed at the higher temperatures. Pure silver was melted in an atmosphere of oxygen in a muffle furnace and poured quickly into water which was kept near 0°. On the resulting material, which was dried in an oven at 90°, three experiments were performed.

Experiment Number 1

Four cylindrical glass tubes containing a capillary tip at the bottom were each filled with about 200 grams of the silver pellets. These were then sealed to a vacuum apparatus and evacuated to a pressure of 0.03 mm. of Hg for two hours. The tubes were then sealed. Two of them were placed in a furnace kept at 400° to 420° for four months. The other two were allowed to stand in a warm place in the room at a temperature of 30 to 35°. The tubes from the furnace stood at room temperature for a month before being opened. The first tube, which contained 217.8 grams of silver, had in it one or two cubic centimeters in excess of 35 cc. of gas. (A small amount was lost in opening.) The second tube (198 g. of silver) contained 35 cc. of gas which analyzed for pure oxygen. One of the tubes which had remained at room temperature for five months was opened by breaking the capillary tip under mercury. About one tenth cubic centimeter of gas was found.

This experiment confirmed those of previous investigators[4] as to the fact that some of the oxygen held in molten silver could be retained at room temperature by rapid cooling, and that this oxygen could be released by heating the silver to a temperature considerably above the temperature of decomposition of silver oxide. (At 403° the pressure of oxygen in equilibrium with silver oxide is 114.5 atmospheres.) The amount so retained (about 1.8 cc. of O_2 at 0° and 760 mm. of Hg for one cc. of Ag) is in agreement with the results of Richards and Wells.

The fact that very little oxygen was released at room temperature, where silver oxide is stable, indicated that the oxygen is retained as silver oxide, for although the diffusion of O_2 through silver is very slight at room temperature and considerable at 400°, the plunged silver is in a porous granular state and so some of the O_2, if retained as such, should have been sufficiently near the surface to have gotten out in five months. From the free energy equation given in Lewis and Randall[6] we can calculate the pressure of O_2 in equilibrium with Ag_2O at room temperature. This is approximately 0.003 atmospheres, which in a free space of about 35 cc. that we had in our tubes gives a volume at one atmosphere of about 0.1 cc.

[6] Lewis and Randall: "Thermodynamics," 481 (1923).

Experiment Number 2

It was hoped that the silver could be dissolved away from the silver oxide or oxygen by means of mercury. An all-glass apparatus was constructed. This consisted of a mercury boiler connected to a water-cooled condenser. This emptied through a small U-shaped trap into a cylindrical vessel. A small tube in the center of this vessel, reaching with an open end almost to the bottom, extended through the side wall and then through a trap into the boiler.

385 grams of the silver were placed in the cylindrical vessel, about 150 cc. of mercury were placed in the boiler, and the apparatus was evacuated, while heating the mercury to a pressure of 0.03 mm. of Hg. The apparatus was then sealed off, and an electric heater placed under the boiler.

In the first day or two a few bubbles of gas came from the silver, and a small pressure developed in the cyclindrical vessel. As the operation proceeded, however, pressure developed in the boiler portion of the apparatus; and frequently the gas from this section would push itself through the small U-trap. In about four and one half months the silver had been entirely dissolved. The apparatus was then taken apart, and the cylindrical vessel examined for silver oxide. It was washed out with concentrated ammonium hydroxide solution, and this solution after neutralization tested for silver ion. None was found.

This experiment indicated that the oxygen in the silver must be in some form slightly soluble in mercury and unstable at a pressure of about 5 cm. of Hg and the temperature at which the mercury was boiling. This probably is silver oxide. Its solubility in mercury is not reported, but this need be extremely small for all of it to be carried over in the four and a half months of the operation.

Experiment Number 3

The third experiment consisted of electrolyzing the silver, hoping to retain the silver oxide at the positive pole. A fairly concentrated silver nitrate solution was used for the electrolyte. This had been put into equilibrium with silver oxide by precipitating a small amount from it with sodium hydroxide solution. 210 grams of the silver was used. The apparatus was an H tube. 0.1 to 0.2 ampere of current was used, and no gas was produced in the cell.

A dark brown deposit appeared in the anode portion. After carefully washing out the electrolyte, this was treated with an ammonium hydroxide solution. After neutralization the silver was precipitated as the chloride and weighed. Calculated as Ag_2O it gave 0.00313 gram Ag_2O per gram Ag. This compares with the result of the first experiment when calculated on the same basis. This is 0.00355 g. Ag_2O per g. Ag.

Discussion

These experiments strongly indicate that the oxygen retained in rapidly cooled silver is in the form of Ag_2O, and that its decomposition has been par-

tially prevented by the rapid cooling. It might be argued that atomic oxygen would react with silver at lower temperatures to produce Ag_2O, and so these experiments not prove that Ag_2O is contained in the silver at the higher temperatures. However, by assuming Ag_2O we can account for all the observed phenomena. The following discussion will prove rather conclusively that it is Ag_2O and not atomic oxygen which is dissolved in silver.

The dissociation pressure of silver oxide has been measured by Lewis[7] and by Keyes and Hara.[8] From these measurements Lewis and Randall[6] have evaluated the equation

$$\frac{\triangle F}{T} = - R \ln K = \frac{\triangle H_o}{T} - 1.0 \ln T + I = - \frac{7240}{T} - 1.0 \ln T + 21.95$$

As $k = \frac{1}{\sqrt{P}}$ for the reaction $Ag + 1/2\ O_2 = Ag_2O$, $- R \ln k = \frac{R \ln P}{2}$.

By inserting constants, etc.

$$\log P = - \frac{3,\ 162}{T} - 1.005 \log T + 9.585.$$

Using this equation to calculate the decomposition pressures at temperatures at which the quantity of oxygen absorbed by the liquid metal has been measured by Sieverts and Hagenacker[1] and assuming Raoult's law to hold for the solution of Ag_2O in Ag, the amount of oxygen absorbed per cubic centimeter or 10.5 grams of silver can be calculated. These values are shown in Table I in comparison to the experimentally determined quantities. The

TABLE I

The Solubility of Oxygen in Molten Silver

Temperature °C	Volume of O_2 absorbed by 10.5 g. Ag cc. at 0° and 760 mm.		Logarithm of the decomposition pressure Calculated from	
	Experiment	Calculated	Experiment	Free energy eqn.
973	20.28	11.73	3.461	3.936
1024	19.53	10.68	3.494	4.019
1075	18.62	9.78	3.544	4.094
1125	17.56	9.05	3.586	4.162

agreement is seen to be good considering the long extrapolation from 500 to 1000° which was necessary in using the equation and also considering the assumption of ideal solution from which considerable deviation would be expected. The agreement is better seen when the logarithms of the decomposition pressures calculated from the amount of oxygen dissolved are compared with the same values calculated by the thermodynamic equation for Ag_2O.

[7] Lewis: J. Am. Chem. Soc., **28**, 139, 158 (1906).
[8] Keyes and Hara: J. Am. Chem. Soc., **44**, 479 (1922).

If atomic oxygen dissolved in molten silver, it would be expected to be absorbed in greater quantities at higher temperatures, for an increase in temperatures would shift the equilibrium $1/2\ O_2 = O$ in the direction of greater quantities of atomic oxygen. The experiments show that the solution of oxygen diminishes with increasing temperature.

Steacie and Johnson[3] have shown that the amount of oxygen taken up by solid silver at constant pressure shows a minimum at about 400°. We can readily account for this phenomenon on the asumption that the oxygen contained in the silver is in the form of silver oxide. The amount of oxygen absorbed would depend upon two effects; first, the solubility of Ag_2O in silver which should increase with increasing temperature, and second, the decomposition pressure of the Ag_2O which increasing with temperature would cause the amount of oxygen to diminish. The interplay of these two effects would give the minimum. At a temperature where Ag_2O is stable at the pressure of O_2 used, the silver would take up oxygen at equilibrium until it were all converted into the oxide. As the temperature is raised, the decomposition pressure increases rapidly, and the amount of oxygen absorbed would correspondingly decrease. Continually raising the temperature, however, increases the solubility of Ag_2O and this effect will gradually overcome the other and cause an increased absorption of the gas with temperature.

From the values given by Steacie and Johnson[3] and the known fact that the amount dissolved varies as the square root of the pressure, the amount dissolved at the silver oxide decomposition pressure can be calculated. From this the true solubility of silver oxide in silver at pressures where silver oxide is stable can be obtained. These values are given in Table II. There is no

TABLE II

Temp. °C	Log decomp. press.	Volume of O_2 absorbed by 10.5 g. Ag at 0° and 760 mm.		Solubility of Ag_2O in Ag (S) g. Ag_2O per 1000 g. Ag	Log. S	Log. S calculated by eqn.
		Experiment Press. = 80 cm.	Calculated at decomp. press.			
200	0.212	0.142	0.177	0.35	$\bar{1}.542$	$\bar{1}.558$
300	1.295	0.097	0.420	0.82	$\bar{1}.914$	$\bar{1}.990$
400	2.044	0.087	0.902	1.78	0.251	0.238
500	2.591	0.095	1.828	3.62	0.558	0.578
600	3.007	0.132	4.102	8.15	0.911	0.917
700	3.332	0.193	8.73	17.5	1.243	1.257
800	3.592	0.354	21.58	44.2	1.646	1.597
923[1]	3.848	0.59	49.66	107	2.029	2.016
		0.54	45.40	97	1.987	

[1] The experimental values at this temperature are given by Sieverts and Hagenacker, the other values are from the work of Steacie and Johnson.

minimum in this solubility curve. It shows a usual behavior for solubility curves in that the logarithm of the solubility increases in a linear manner with the temperature. The equation representing this is log $S = 0.0034$ $(t - 330)$, in which S is the solubility of silver oxide in grams per thousand grams of silver and t is the temperature in °C.

Summary

Experiments are described which indicate that the oxygen retained by rapidly cooled silver is in the form of silver oxide.

The assumption that the oxygen dissolved in silver is in the form of silver oxide has been used to explain the solution of oxygen in molten silver and in solid silver. An agreement with experimentally determined quantities has been obtained in the case of molten silver, and the minimum solubility at 400° in solid silver has been explained.

The solubility curve of silver oxide in solid silver has been calculated.

It is concluded that oxygen dissolves in silver in the form of silver oxide and not as atomic oxygen.

Evanston, Illinois.

CONSTANT-EVAPORATION SYSTEMS*

BY ERNEST ROBINSON, W. ANDREW WRIGHT, AND GEORGE W. BENNETT

The phenomenon of azeotropism has been known to physical chemists for some time, but the related phenomenon of constant-composition evaporation mixtures is not mentioned frequently in the literature although Keyes[1] gives the impression in his book review of "Solvents" that chemists are generally aware of such systems. Hofmann and Reid[2] have drawn attention to the existence of such systems, and have indicated their significance in the formulation of lacquers. These investigators found that alcohols and hydrocarbons form a number of systems each of which has a definite composition at a given temperature which remains invariant during the evaporation of the mixture. Sunier and Rosenblum[3] in a paper devoted to a discussion of physical methods for the separation of constant-boiling mixtures indicate that a study of the evaporation of liquid mixtures by sweeping away the vapors with an inert gas might throw important light on the feasibility of separating azeotropes. This proposal needs to be considered in the light of possible systems such as Hofmann and Reid have observed. Roscoe[4] apparently was the first to report the phenomenon of constant-composition evaporation mixtures. The effect was observed many times in his studies on constant-boiling solutions of acids, so that he was led to state that "the composition of a constant-evaporating mixture at a given temperature is identical with the composition of a mixture boiled at such a pressure as to give the same temperature by boiling." Many investigators have traced the shift in azeotropic composition at the boiling point with change in pressure, in which case, to them the corresponding temperature was a secondary matter.

Method of Study

The method of investigation described by Hoffman and Reid was soon found unsatisfactory due to a considerable condensation of atmospheric moisture in the binary systems. The procedure as finally developed utilized a train of apparatus with the following parts: (1) drying towers for the incoming air, (2) the evaporation flask immersed in a water thermostat, (3) a flow-meter, (4) drying towers, (5) a Victor Meyer hydrostatic pressure regulator modified to permit suction, and (6) the aspirator.

[1] D. B. Keyes: Ind. Eng. Chem., **22**, 1412 (1930).

[2] Hofmann and Reid: Ind. Eng. Chem., **20**, 687 (1928).

[3] Sunier and Rosenblum: Ind. Eng. Chem. Anal. Ed., **2**, 109 (1930).

[4] Roscoe and Dittmar: J. Chem. Soc., **12**, 128 (1860); Roscoe: **13**, 146 (1861); **15**, 270 (1862); **16**, 82 (1863).

The evaporation flask was equipped with (1) a sampling tube reaching into the liquid which could be operated by (2) an outlet for applying air pressure, closed by a pinch-clamp when not in use, (3) a thermometer reaching into the liquid, and (4) a manometer for ascertaining the pressure within the flask during an experiment. This set-up gave rather close control of the volume and humidity of the entering air as well as of the temperature of the evaporation vessel.

The materials used were all "Eastman" grade chemicals, or else laboratory reagents purified as necessary for each liquid. Their purity was checked by boiling points and refractive indices. Appropriate mixtures of the several binary systems were placed in the flask, and a current of air was then aspirated through the train. At half hour intervals the flask was shaken to mix the contents thoroughly, and a small portion of the mixture was withdrawn for analysis. The rate at which air was drawn through the apparatus was dependent on the rate of evaporation of the system being examined, but it was so modified as to require three hours for each evaporation.

The samples were brought to 20°C and the refractive index determined by the Abbe refractometer. For the mixtures having the constant composition the refractive index remained unchanged during a three to four hour period (or longer, depending on the volume of liquid being evaporated). This refractive index was referred to a refractive index-composition curve for each system, and the composition of the sample was read from the reference curve. Mixtures not at the constant composition gave refractive index-time curves that curved away towards the values of the refractive indices of the pure components for the minimum-boiling type of azeotrope, while curves for the maximum-boiling type sloped in towards the refractive index of the constant evaporation mixture. The azeotropic compositions at the boiling points were determined when the distillate and residue gave the same refractive index.

Among other results obtained was sharp evidence for azeotropism in the system methanol-toluene although Lecat[1] confirms other investigators that azeotropism does not exist in this system. A later paper by Lecat[2] on azeotropism in alcohol-hydrocarbon systems failed to mention this pair of liquids. Certain of the azeotropic compositions at the boiling point as given by Lecat also differed from values obtained by us. In each case determinations were repeatedly made, and the liquids carefully checked to insure purity.

The results obtained by this experimental procedure are summarized in the Table, and expressed graphically in the two figures. In the Table the numbers in the first column serve to identify, on the two graphs, the systems listed in column two. In column three the several evaporation temperatures are given. In column four values are given for the mol fraction (N_1) of the first-named constituent in column two as found in the constant evaporation mixture. The last column gives values for the ratio of mol fractions of the two constituents in the constant evaporation mixtures.

[1] Lecat: "L'Azéotropisme," 101 (1918).
[2] Lecat: Ann. soc. sci. Bruxelles, **48B** II, 105 (1929).

In Fig. 1 the azeotropic concentrations, expressed in mol fractions of the first-named constituent in column two of the Table, are plotted against the temperatures under which the evaporations were made. In Fig. 2 the ratio of the mol fractions of the two constituents of the several systems are plotted as a function of the temperatures under which the evaporations were made. In both figures the numerals on the several curves refer to the systems listed and numbered in Table I.

TABLE I

No.	System	Temp.	N_1	N_2/N_1
1.	Toluene-Methyl alcohol	0.5	0.122	7.20
		25.0	0.114	7.77
		50.0	0.109	8.17
		62.5	0.104	8.61
2.	Toluene-Ethyl alcohol	0.5	0.368	1.72
		25.0	0.2695	2.71
		50.0	0.216	3.63
		75.5	0.182	4.49
3.	Toluene-n-Propyl alcohol	0.5	0.728	0.373
		25.0	0.613	0.632
		50.0	0.507	0.973
		71.1	0.438	1.28
		91.1	0.389	1.57
4.	Toluene-n-Butyl alcohol	0.5	0.931	0.074
		25.0	0.927	0.079
		50.0	0.913	0.095
		73.0	0.860	0.163
		103.1	0.673	0.485
5.	Xylene-n-Butyl alcohol	20.0	0.624	0.602
		40.0	0.528	0.892
		60.0	0.436	1.294
		80.0	0.350	1.867
		115.0	0.207	3.828
6.	Toluene-iso-Propyl alcohol	20.0	0.417	1.400
		40.0	0.314	2.186
		60.0	0.240	3.124
		78.0	0.193	4.180
7.	Benzene-Methyl alcohol	20.0	0.424	1.357
		40.0	0.408	1.450
		57.0	0.394	1.538
8.	Chloroform-Methyl acetate	20.0	0.591	0.692
		40.0	0.615	0.626
		63.3	0.650	0.539
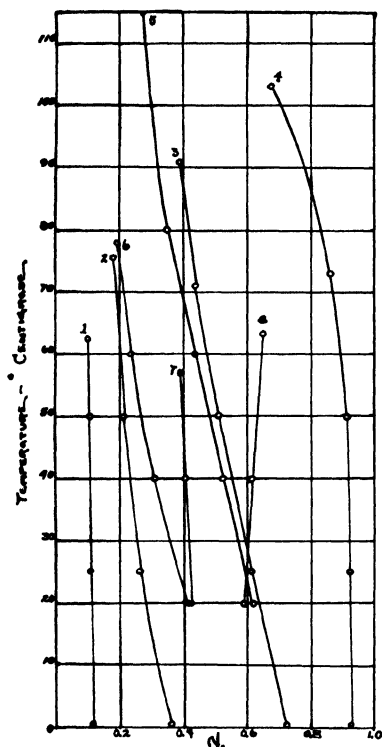
FIG. 1

Shift of Azeotropic Point with
Temperature
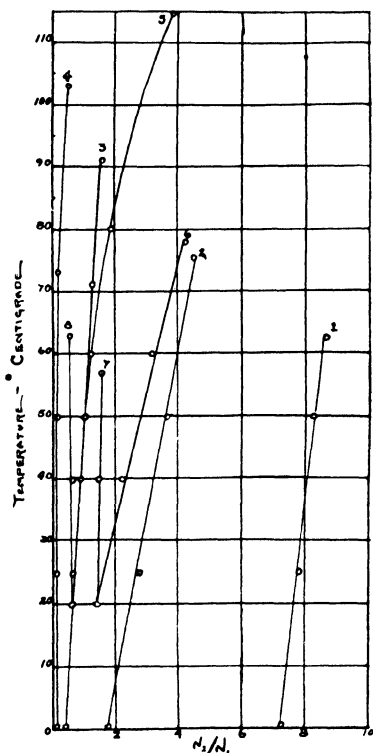
FIG. 2

Effect of Temperature on Mol
Fraction Ratio

Discussion

From the graph for the change of the constant composition with the temperature it is plain that there is a continuous shifting of this composition from the boiling point of the azeotropic mixture to room temperatures and below. It is apparent, therefore, that constant evaporating mixtures are directly related to constant-boiling mixtures, and that it is untrue that the two phenomena are similar but unrelated. It is important to state this fact because several writers seem to have been under the impression that the two manifestations of azeotropism are not directly related phenomena.

It is to be observed that the slopes of the curves relating azeotropic composition to the temperature are of such a nature that the pure constituents are not rapidly approached as the temperature is lowered. If the systems here studied are typical it follows, then, that the phenomenon of constant-composition evaporation must be a very wide-spread phenomenon—almost as extensive, perhaps, as the field of azeotropism itself. Indeed the exceptions that Young[1] Konovaloff,[2] Merriman[3] and Wade and Merriman[4] have been

[1] Young: J. Chem. Soc., **81**, 717 (1902).
[2] Konovaloff: J. Chim. phys., **5**, 1-28, 237-262 (1905).
[3] Merriman: J. Chem. Soc., **103**, 628 (1913).
[4] Wade and Merriman: J. Chem. Soc., **99**, 997 (1911).

able to present against van der Waals'[1] conclusion that azeotropism exists from the critical temperature to the temperature of congelation, are very few.

A study of the shift in azeotropic composition by the method outlined in this paper has several advantages over the method of altering the pressure on a system. In the first place the change of pressure necessary to produce even a moderate change in the azeotropic temperature may be very great. In the second place the difficulties attendant on barostatic control are much greater than those of thermostatic control. It is possible also, to carry out a complete experiment without interruption or altering the conditions under which it is being performed. And again, it has been possible to study systems over a much wider range of azeotropic temperatures than is commonly possible under diminished pressures. As a matter of fact it is the temperature which controls the partial pressures of the constituents, and hence the composition of the mixture, rather than the pressure under which the azeotrope boils. More than one author, however, has stated or implied that a constant-boiling mixture has a definite composition which is dependent only on the pressure.

This point of view seems to have developed due to the emphasis on the study of azeotropic composition as a function of the pressure. The early investigators carried out evaporations at the point of ebullition, i.e., under one given pressure which was equal to the vapor pressure of the system. This vapor pressure is, however, a function of the temperature. If then the pressure is fixed, the temperature becomes a dependent factor, and one might put emphasis on the former rather than on the latter. When, however, the pressure on the system is greater than its own vapor pressure there is no need to suppose, a priori, that azeotropic mixtures cannot exist. It seems more reasonable to say then, that an azeotropic mixture has a definite composition dependent only on the temperature under which it boils (or evaporates).

The data obtained in the present study throw interesting light on the proposals of Sunier[2] and of Sunier and Rosenblum (loc. cit.) for the separation of azeotropes by physical methods. Under conditions of non-equilibrium evaporation separation of the constituents may be expected to follow the Sunier equation

$$\frac{w_1}{w_2} = \frac{p_1}{p_2}\sqrt{\frac{M_1}{M_2}}$$

where w_1 and w_2 are the weights of the constituents removed per second per square centimeter of surface, p_1 and p_2 their respective partial pressures and M_1 and M_2 the molecular weights of the two constituents. One might well question if non-equilibrium evaporation could be produced by diminishing the pressure over the binary mixture as the investigators suggest, for if the pressure is lowered sufficiently ebullition will take place, and equilibrium conditions will be reached. If the pressure can be lowered to such a point that azeotropism disappears, as for instance in the case of ethyl alcohol-water[3] then

[1] Van der Waals: "Die Kontinuität des gasförmigen und flüssigen Zuständes" (1900).

[2] Sunier: J. Chem. Educ., 5, 879 (1928).

[3] Merriman: loc. cit.

the system becomes zeotropic, and hence may be resolved. If, however, the constant-boiling mixture is allowed to evaporate without ebullition at some other temperature, a different result is obtained. The mixture which was azeotropic at the boiling point now consists of an azeotrope of another composition and an excess of one of the pure constituents. The mixture at best can be resolved only into the new azeotrope and the pure constituent. The extent of such resolution is dependent, not on the change in the partial pressures with the temperature, but on the change in the ratio of p_1/p_2, for although the vapor pressures of pure liquids change at different rates with the temperature there is no assurance that the relative partial pressures of the constituents of a mixture will be different at several temperatures. In the cases of methanol-toluene, methanol-benzene, and n-butyl alcohol-toluene (below $75°$) the azeotropic composition and hence the ratio of partial pressures, has evidently not changed materially. Even where there is a material change in the ratio of the partial pressures, success of resolution will depend on the nature of the boiling point curves in that leg of the phase diagram in which the excess of pure constituent occurs.

The qualitative nature of the shift in azeotropic composition has been formulated by several authors, but perhaps best by Merriman,[1] Wrewsky,[2] and Tanaka and Kuwata.[3] As far as we can learn, however, no one has attempted any quantitative expression of this change in azeotropic composition. For those systems studied by us the ratio of the mol fractions as a function of the temperature can be represented by the expression

$$N_2/N_1 = At + B$$

and in a few cases by

$$N_2/N_1 = At^2 + Bt + C$$

where A, B, and C are constants. Further work to test the applicability of this expression is being carried out in this laboratory.

Grove City College,
Grove City,
Pennsylvania.

[1] Merriman: J. Chem. Soc., **103**, 1790 (1913).
[2] Wrewsky: Z. physik. Chem., **83**, 551 (1913).
[3] Tanaka and Kuwata: Chem. News, **137**, 13 (1927).

PHOTOLYSIS OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE

BY M. QURESHI AND M. K. RAHMAN

The photo-chemical decomposition of hydrogen peroxide in ultra-violet light has been investigated by a number of workers. Tian[1] studied the kinetics of the reactions in the light of a mercury lamp and came to the conclusion that the reaction follows a unimolecular course. The same author[2] further found that the reaction velocity is proportional to the intensity of light. Henri and Wurmser[3] determined the quantum efficiency of the reaction in two sets of experiments. In the first, using full light from a cadmium spark, the value for the quantum efficiency (γ) was found to be nearly 130. In the second, where monochromatic light was employed, much lower values ranging between 4.4 and 5.8 were obtained. The reaction velocity was found proportional to the intensity. Kornfeld[4] employing a radiation of wave-length 311 mμ and solutions of different concentrations, found values of γ between 7 and 80. Quantum efficiency in these experiments was found to increase with increasing concentration of hydrogen peroxide. Winther[5] attributed the difference in the values of γ found by Kornfeld and Henri and Wurmser to the effect of light intensity. Kornfeld obtained a quantum efficiency of 43.2 with a solution of concentration .049 N and radiation of wave-length 311 mμ where as Henri and Wurmser's value extrapolated for the same concentration and wave-length is 2.9. This discrepancy, according to Winther, may be due to lack of proportionality between reaction velocity and intensity, assuming that all other conditions excepting light intensity in the two experiments are the same. The work of F. O. Rice[6] established the presence of dust particles as an important factor in the photochemical decomposition of hydrogen peroxide, by showing that the rate of decomposition is proportional to the dust content as measured by the light scattering power of the solution. In the opinion of this author, the true quantum efficiency of the reaction is very much lower than the values actually found by Kornfeld and Henri and Wurmser. In the complete absence of dust it should be unity. Quite recently, Allmand and Style[7] have made a thorough experimental study of the reaction. The results of their experiments indicate that over wide ranges of intensity, wave-length and concentration, the rate of photolysis is proportional to the square root of intensity. At very high

[1] Compt. rend., **151**, 1040 (1910); **156**, 1601, 1758, 1879 (1913).
[2] Ann. Phys., **5**, 248 (1916).
[3] Compt. rend., **156**, 1012 (1913); **157**, 126, 284 (1913).
[4] Z. wiss. Phot., **21**, 66 (1921).
[5] Trans. Faraday Soc., **21**, 459 (1926).
[6] J. Am. Chem. Soc., **98**, 2099 (1926).
[7] J. Chem. Soc., **1930**, 596.

and low concentrations, however, and with low intensities, the rate tends to be proportional to the intensity. The velocity of decomposition at constant incident intensity, as also the quantum efficiency, increases with the concentration of hydrogen peroxide, passes through a maximum and then falls off.

The present investigation was undertaken with a view to (a) ascertain the influence of intensity on the rate of photolysis and (b) determine the quantum efficiency at different concentrations. It was commenced before the publication of Allmand and Style's work. The results, as far as the influence of light intensity is concerned, confirm the main conclusion of these authors, namely that the rate of photolysis is proportional to the square-root of the intensity.

Experimental

Aqueous solutions of hydrogen peroxide were exposed in a reaction-vessel of quartz with plane-parallel sides and the extent of decomposition was
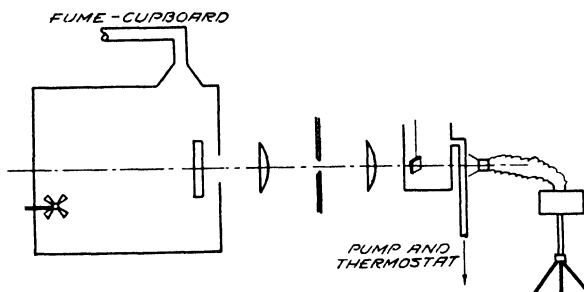
FIG. 1

determined by pipetting out measured quantities and titrating against potassium permanganate solution (N/100). The rate of thermal decomposition was measured simultaneously at the same temperature and deducted from the total decomposition in light. For the purposes of the former, small flasks painted black from outside were used. Every possible precaution was taken to exclude dust particles from solutions. The room in which these experiments were conducted was isolated from the rest of the laboratory. The vessels used were of Jena glass. After being cleaned, steamed, and washed with conductivity water, they were stored in a cupboard in the same room. In all washings and preparations of solutions conductivity water of the highest purity was used. The burette used for titration was graduated to 0.02 c.c and certified by the National Physical Laboratory. The titrations were conducted in the light of a small electric lamp, placed in a corner of the room away from the thermostat. The standard solution of permanganate was stored in a bottle covered with black paper. The arrangement of the apparatus used in these experiments is shown in Fig. 1. The reaction vessel was placed in a small rectangular bath, having two quartz glass windows on opposite sides. Into this bath, water was pumped by means of a centrifugal pump from a thermostat placed below. There was an overflow opening

near the top of the small bath which allowed water to go back to the thermostat. The temperature of the main thermostat was kept constant as usual by means of toluene regulator and an electric relay. In this way it was found possible to regulate the temperature of water in the quartz bath within 1/10th of a degree. The source of light used was the mercury vapour lamp manufactured by Heraeus in Hanau, which was worked on 230 volts A.C. The lamp was placed in a wooden box specially improvised for the purpose and lined inside with asbestos. A small electric fan placed inside the box served to ventilate the box. The ozonised air was forced through an outlet on the top of the box into a chimney connected to a fume cupboard. The light from the lamp passed through an opening in the side of the box, provided with a diaphragm, and was converted into a parallel beam by means of a system of quartz lenses before it reached the reaction vessel.

The measurement of light energy was carried out by means of a thermopile and a loop galvanometer made by Carl Zeiss. The sensitiveness of this galvanometer per scale division of the eye piece at 80 magnification and in its stable position is about 3×10^{-7} amps. and its internal resistance 6–10 ohms. The method adopted for the energy measurement will be described later.

Merck's 30% perhydrol prepared for the tropical countries was used. Solutions were made with conductivity water especially prepared for the purpose.

Effect of Light Intensity

Two sets of experiments were performed for determining the effect of light intensity on the rate of decomposition of hydrogen peroxide.

In the first set of experiments the intensity was varied by means of a rotating sector, placed between the source of light and the reaction vessel. The sector was rotated by means of an electric motor at the speed of 200 revolutions per minute. The amount of hydrogen peroxide decomposed in one hour with different sector opening was determined by titration against $N/100$ permanganate. Temperature was regulated at 30°C.

TABLE I

Method of Rotating sector,
Velocity of rotation = 200 revolutions per minute.
Concentration of the solution 0.1 molar nearly.
Temperature 30°C.

Sector Angle	Relative intensity	Amount of hydrogen peroxide decomposed in c.c.'s of permanganate solution $N/100$	Rate of decomposition intensity	Rate of decomposition $(intensity)^{0.5}$
45°	1	0.270	0.270	0.270
90°	2	0.368	0.184	0.260
180°	4	0.622	0.156	0.310
360°	8	0.800	0.100	0.280

In the second set of experiments the intensity was varied by changing the aperture of the diaphragm. In these experiments the whole of the light emerging from the aperture was made to fall on the reaction vessel and the amount of hydrogen peroxide decomposed per hour with different apertures was determined as before. The temperature was kept constant at 30°C. The results of these experiments are given in Table I.

TABLE II

Method:—Variation of diaphragm opening.

Concentration—0.1 molar.

Temperature = 30°C.

Diameter of aperture in cm.	Relative intensity	Hydrogen peroxide decomposed in c.c.'s of permanganate solution N/100	Rate of decomposition intensity	Rate of decomposition (intensity)$^{0.5}$
2.5	1	0.435	0.435	0.43
5.0	4	0.660	0.165	0.33
7.5	9	0.826	0.09	0.28

Quantum Efficiency at Different Concentrations

In these experiments a quartz cell with plane parallel walls was used. 15 c.c. of hydrogen peroxide solutions were used in each case. The strength of hydrogen peroxide was determined by titrating against standard potassium permanganate immediately before and after exposure. The difference gave the amount decomposed. The cell was placed as described before in a small bath with quartz windows on opposite sides. The light from the quartz lamp after passing through the cell and the bath fell upon a thermopile placed immediately behind the bath and connected with a loop galvanometer (Carl Zeiss) having an internal resistance of 6–10 ohms and sensitiveness of 3×10^{-7} amps. The calibration of the galvanometer was carried out both before and after the experiments by means of a standard Heffner lamp. This lamp, burning amyl acetate under standard conditions and placed at a distance of one meter from the thermopile, produced a deflection of 2.88 in the galvanometer. Taking Gerlach's[1] value of 900 ergs per sq. cm. per second for the energy obtainable from a Heffner lamp at a distance of one meter a deflection of one scale division is equivalent to $900/2.88$ ($= 312.5$) ergs per sq. cm. per second. For measuring the amount of energy absorbed by hydrogen peroxide. Deflection was noted first with water and then with a solution of hydrogen peroxide in the quartz vessel. The difference of the two deflections corresponds to the energy absorbed by hydrogen peroxide. The ratio of the number of molecules of hydrogen peroxide decomposed per second in light as determined by titration against standard potassium permanganate to the number of light quanta absorbed gives the quantum efficiency of the reaction. It must be noted that in calculating the molecules

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[1] Physik. Z., **14**, 577 (1913).

of hydrogen peroxide decomposed by light alone, the amount of hydrogen peroxide decomposed in the dark in a control experiment was deducted from the total amount decomposed in light. In calculating the number of light quanta the average wave-length of the effective rays was taken as 313 mμ. The results of calculations are shown below. Temperature was kept constant at 30°C.

TABLE III

Molar concentration	Quantum efficiency	Molar concentration	Quantum efficiency
0.9	7.31	0.09	10.92
0.45	7.90	0.03	4.86
0.3	7.98	0.01	2.76

Discussion

The results of our experiments on the influence of intensity (Tables I, II) indicate that with solutions of 0.1 M. concentration the rate of photolysis is proportional to the square root of the light intensity. Allmand and Style have also obtained the same relation, using dilute solutions of Merck's perhydrol, containing a thermal inhibitor; although from other experiments in which an inhibitor-free perhydrol was employed, the same authors conclude that at high and low concentrations (11.5 M. and 0.48 M.) the velocity of photo-chemical decomposition tends to be proportional to the intensity. The square-root relation is explained by these authors on the assumption that the hydroxyl groups or oxygen atoms formed by the primary action of light accumulate in the liquid phase and disappear when their rate of production per unit volume is sufficiently high. In order to explain the validity of the simple relation at high and low concentrations a further assumption involving the existence of unstable complexes (H_3O_3) is found necessary. This theory of mechanism appears to be satisfactory in certain respects, but as the authors themselves point out, it does not explain all the experimental data. One such instance in which the above-mentioned mechanism fails to account for the experimental results is the behavior of dilute solutions below 1.8 molar concentration. In some of their experiments with dilute solutions the quantum efficiency is found to drop continuously with decrease in concentration, while in other it first increases, passes through a maximum and then falls off as the concentration decreases. The results of our experiments on the measurement of quantum efficiency at low concentrations (Table III) show a similar falling off after passing through a maximum. It may be pointed out that Kornfeld also found a drop in the value of γ from 80 to 24 as the concentration decreased from 0.5 N to 0.016 N. Obviously more experiments in this direction are desirable before a satisfactory explanation of the mechanism of this reaction could be constructed. The results of further work by Allmand and Style will be awaited with interest.

Summary

(1). The influence of light intensity on the rate of photolysis of aqueous solutions of hydrogen peroxide has been measured by the methods of rotating sector and the variation of diaphragm opening. The results obtained by both the methods indicate that the rate of photolysis is proportional to the square root of the intensity: Solutions of 0.1 M. concentration were employed.

(2). Quantum efficiency γ of the reaction has been determined at various concentrations, with the help of a thermopile and loop galvanometer (Carl Zeiss). The value of γ at first increases as the concentration of H_2O_2 decreases, passes through a maximum, and then falls off. It varies between 11 and 3.

(3). Further work, particularly on dilute solutions, is desirable before any satisfactory theory of the mechanism could be advanced.

Department of Chemistry,
Osmania University College,
Hyderabad-Deccan, India,
August 14, 1931.

THE THERMAL DECOMPOSITION OF ISOPROPYLAMINE

BY H. AUSTIN TAYLOR

Previous investigations on the pyrolysis of aliphatic amines[1] have shown that the series offers useful and interesting examples of homogeneous unimolecular reactions. These have been shown to possess a simplicity to be contrasted with the complexities observed in ether decompositions in that activation appears to be concerned only with a single vibrational bond, corresponding that is, to two square terms. It has been suggested that the rupture is most probably in the C-N bond. This would infer as was suggested in the previous papers that at the temperatures employed the initial reaction involved a direct splitting out of ammonia. The alternative mechanism suggested by Hurd and Carnahan[2] involves a loss of two molecules of hydrogen resulting in a nitrile formation. The probability of such an occurrence would be considerably reduced with an iso-amine in comparison with a normal straight chain compound. Disregarding the fact that the effect of added hydrogen on the decompositions of ethylamine and propylamine has been shown not to be in agreement with the nitrile mechanism, the similarity between the kinetics of the iso-propylamine decomposition here studied and the previous results would itself infer the inaccuracy of such a mechanism. It is unfortunate that the subsequent reactions of the unsaturated hydrocarbons formed by the removal of ammonia from the amines proceed at a rate which complicates the study of what now appears definitely to be the simple rupture of the C-N bond.

The similarity of the results found for isopropylamine with those for propylamine do not warrant any extended account being given. The apparatus and procedure were identical with those already published. The temperature range used was from 490°C to 540°C. Pressures from about 15 mms. to 220 mms. were used. The pressure increase during reaction was somewhat greater than for propylamine, being on the average 130 percent.

The unimolecular nature of the reaction is shown in a typical case by the data in Table I showing a constant quarter life at pressures above 150 mms. with increasing values corresponding to slower reaction at successively lower pressures.

TABLE I

Temperature 495°C

Initital Pressure	Quarter Life	Initial Pressure	Quarter Life
218.5 mms.	2.0	70	2.25
187.4	2.0	36	2.4
160	2.0	17	2.5
110.5	2.2		

[1] J. Phys. Chem., **34**, 2761 (1930); **35**, 2658 (1931).
[2] J. Am. Chem. Soc., **52**, 4151 (1930).

The absence of heterogeneity is typified in Table II giving a comparison of the actual pressure changes obtained using an empty pyrex bulb and one partly filled with pyrex powder.

TABLE II

Temperature 495°C

Initial Pressure Time	Empty Bulb 218.5 mms. $\triangle P$	Pyrex Powder 229 mms. $\triangle P$	Initial Pressure Time	Empty Bulb 218.5 mms. $\triangle P$	Pyrex powder 229 mms. $\triangle P$
0.5 mins.	32 mms.	26 mms.	6	138	141
1	50	45	8	158	159
2	76	73	10	173	173
3	96	95	15	208	205
4	111	113			

In Table III are given comparative data for the pressure changes obtained in presence of 200 mms. of added hydrogen and nitrogen.

TABLE III

Temperature 495°C

Initial Pressure of Amine Time in mins.	160 mms. $\triangle P$	Hydrogen 169 mms. $\triangle P$	Nitrogen 163 mms. $\triangle P$
0.5	21	20	20
1	36	34	33
2	56	54	53
3	68	69	67
4	81	82	78
6	98	103	95
8	111	117	110
10	122	130	123
15	144	154	147
20	161	173	164
25	175	188	174
30	185	198	190

The obvious similarity of the course of the reaction in these cases is confirmation of the unimolecular nature of the reaction. The effect of added hydrogen at intial pressures of amine below 150 mms. where the decomposition is no longer unimolecular is similar to its effect in the ether decompositions in its ability to maintain the reaction at its first order rate. For example from Table I it can be seen than an initial pressure of amine of 47 mms. would possess a quarter life of 2.3 mms. when decomposing alone. It was found that at the same temperature of 495°C, 47 mms. of amine in presence of 186 mms. of hydrogen decomposed 25 percent in 2.0 mins., the value of the quarter life at higher pressures of amine in the absence of hydrogen.

The time of quarter decomposition has been used in the above considerations as the criterion of the rate of reaction for reasons similar to those mentioned in the previous works. The lack of constancy of the times of 50 and

75 percent decomposition due to secondary reactions is reflected in the falling values obtained for the unimolecular velocity constants calculated for each case examined. The behaviour is again similar to that found with propylamine. A typical example is given in Table IV.

TABLE IV
Temperature 530°C

Time	$\triangle P$	k	Time	$\triangle P$	k
0.5	66	0.517	6	225	0.249
1	102	0.434	8	245	0.233
1.5	127	0.384	10	259	0.224
2	146	0.349	15	277	0.207
3	173	0.303	20	288	0.249
4	195	0.279			

The values of the quarter lives of the reaction in the stable region of pressure at different temperatures are given in Table V.

TABLE V

Temperature	490	495	500	510	520	530	540°C
Quarter Life	2.5	2.0	1.7	1.2	0.9	0.6	0.45 mins.

The logarithms of these times plotted against the reciprocals of the absolute temperatures yield a straight line with a slope corresponding to an energy of activation of 42,600 calories. This value is somewhat less than the 44,400 calories obtained for propylamine, which was to be expected since an extrapolation of the above data shows the isopropylamine decomposition to proceed at 480°C at the rate attained by propylamine at 500°C. At this temperature of 480°C the value of E/RT is 28.4 as compared with values of 28.2 for ethylamine and 28.9 for propylamine at comparable temperatures.

The final point of similarity lies in the agreement between the calculated ratio of effective to total collisions at the pressure where the reaction ceases to be unimolecular and the value of $e^{-E/RT}$. Since the reaction deviates from its unimolecular course below 150 mms. there will be at 480°C. approximately 2×10^{27} collisions per cc. per second. The number of molecules reacting is 4×10^{15} giving a ratio of 2×10^{-12}. The value of $e^{-E/RT}$ is 4.6×10^{-13}, yielding an agreement which could be expected only if a single bond involving two square terms was responsible in the activation process for the isopropylamine as found previously for propylamine. Further work on di- and trialkyl amines is in progress.

Summary

The pyrolysis of isopropylamine has been shown to parallel that of propylamine as a homogeneous reaction, unimolecular at pressures higher than 150 mms. and possessing an energy of activation of 42,600 calories accountable on the basis of an activation and rupture of a single vibrational bond probably between the carbon and nitrogen.

Nichols Chemical Laboratory,
New York University, New York, N. Y.

SOLID POLYIODIDES OF POTASSIUM*

BY H. W. FOOTE AND WALTER M. BRADLEY

The literature of this subject has been summarized quite recently in two papers[1] which appeared almost simultaneously while our own work was in progress. The conclusions in the two papers are somewhat at variance, particularly in regard to compound formation from water solution.

It has been shown by Briggs and Geigle[2] that the two components, potassium iodide and iodine, exhibit a simple fusion diagram and that no polyiodide forms at temperatures where fusion occurs. At lower temperatures, probably the simplest way to determine whether a polyiodide forms or not is to introduce a liquid component and determine the solubility relations. If the liquid component does not enter into the composition of the solid phases, the solubility results are sufficient to show whether or not a two-component polyiodide can exist at the temperature of experiment. Using the solvent tetrachlorethane, Grace has concluded that potassium iodide and iodine do not form a binary addition product at $25°$.

The liquid component may, however, unite with the others to form a solvated ternary addition product, when no binary compound exists. The results of Grace, at $25°$, indicate that water forms two such hydrated addition products, while Bancroft, Scherer and Gould, with less experimental evidence, claim that no addition products of any kind form in this system. Benzene also forms such a ternary compound, which we shall discuss in more detail below.

We have determined two solubility isotherms in each of the three systems of potassium iodide and iodine with toluene, chloroform, and benzene. Our results with the first two solvents confirm the results of Grace that potassium iodide and iodine form no two-component addition product at $25°$, and extend this conclusion to $0.7°$. With benzene, we have found, as did Grace, that a ternary compound exists, but our results do not confirm the composition of the compound found by him.

Materials and Methods

The three solvents, toluene, chloroform, and benzene were dried over phosphorus pentoxide and distilled before use. Potassium iodide and iodine were of suitable purity and were merely dried thoroughly.

In each system, weighed amounts of the three components in varying proportions were introduced into bottles with specially ground stoppers. Before placing the bottles in the thermostat, the stoppers were coated with

[1] Bancroft, Scherer and Gould: J. Phys. Chem., 35, 764 (1931); N. S. Grace: J. Chem. Soc., 1931, 594.

[2] Briggs and Geigle: J. Phys. Chem., 34, 2250 (1930).

a quick-drying enamel which was not attacked by the three solvents used, and then dipped in melted paraffin, to make certain that no water entered the bottles from the thermostat. As potassium iodide is extremely insoluble in all three solvents, it was anticipated that equilibrium might be reached slowly if addition products formed. The two solids were therefore finely pulverized and either glass pearls, glass rods, or pieces of broken porcelain introduced in the bottles to promote reaction between the solids and prevent lumps from forming. This precaution was probably only necessary with the benzene solutions. The broken porcelain was preferable to the glass pearls or rods. With porcelain we never found any difficulty in reaching equilibrium after three days of shaking, though most of the experiments ran considerably longer. Solutions for analysis were removed through a filter of glass wool and iodine determined in the weighed sample by titrating with sodium thiosulphate. Preliminary determinations showed that the amount of potassium iodide in all solutions was negligible.

To determine the composition of the solid residues in equilibrium with the solutions, either of two methods was used, depending on conditions. In the systems with toluene and chloroform, qualitative tests showed that the residues were not solvated and the composition of the residues could be obtained, either graphically or by calculation, when the composition of the solution and the gross composition of the original mixtures were known. In the system containing benzene, the composition of those residues which consisted of the pure compound alone was always obtained by analysis. The Schreinemakers method of analyzing wet residues was unsuitable in this case on account of the position and form of the solubility curve. The empirical composition of mixtures of two solids in this system could be determined graphically with sufficient accuracy as in the other systems, when the composition of the addition product was known.

The isotherms at 0.7° and at 6° were carried out in a low-temperature thermostat which has recently been described.[1]

Following are the results with toluene and chloroform. All data represent per cent by weight.

System: $C_6H_5CH_3–KI–I_2$

Temperature, 25°		Temperature, 0.7°	
% I_2 in Solution	% I_2 in Residue	% I_2 in Solution	% I_2 in Residue
15.89	98.04	9.12	94.47
15.93	91.04	9.11	90.59
15.76	82.56	9.15	50.70
15.76	54.02	9.10	40.66
16.01	35.14		
15.88	8.25		

[1] Foote and Akerlof: Ind. Eng. Chem., Anal. Ed., **3**, 389 (1931).

System: $CHCl_3$–KI–I_2

Temperature, 25°		Temperature, 0.7°	
% I_2 in Solution	% I_2 in Residue	% I_2 in Solution	% I_2 in Residue
2.95	95.54	1.20	95.47
2.99	90.13	1.21	90.95
2.98	56.08	1.28	54.62
2.97	21.18	1.20	14.77

The constant solubility with widely varying residues shows that potassium iodide and iodine form no two-component addition product at either temperature investigated. The results at 25° confirm those of Grace obtained with tetrachlorethane.

System: C_6H_6–KI–I_2.—This system was first investigated by Abegg and Hamburger[1] who showed by solubility determinations that one or more addition compounds formed. They had difficulty in reaching equilibrium, however, and did not suspect that a solvated compound formed. Grace has recently investigated the system again and found one ternary addition product. He analyzed only one sample of the compound, and derived the formula $KI \cdot 3I_2 \cdot 2C_6H_6$. Our own investigation was well advanced when the work of Grace appeared, and as our results did not entirely agree with his, we have taken some care to corroborate them. We found at 25° and 6° that only one addition product forms, but it appears to have the composition $KI \cdot 4I_2 \cdot 3C_6H_6$.

A series of solubility determinations at 6° and 25° on mixtures of the components in widely varying proportions showed that at both temperatures there were two univariant systems. As the gross composition of each original mixture was known, the ratio of potassium iodide to free iodine in each residue could be determined graphically with sufficient accuracy after the composition of the addition product had been determined by analysis. We give below (Table I) the results obtained. The solubility shows the parts by weight of iodine in 100 parts of solution, and the molecular ratio gives the ratio of free iodine to potassium iodide in the residues. The residues also contained benzene of crystallization due to the presence of the addition product which was present in all residues.

The data in Table I show, at each temperature, that a solid addition product exists, but appear to exclude the possibility of a solvated compound in which the ratio of $KI : I_2$ is 1:3, which is the ratio found by Grace.

To obtain the composition of the pure addition product, a series of mixtures was prepared in such proportions that the solubility fell between the two univariant points. After analyzing the solutions, the solids were rapidly freed from adhering solution by pressing between filter paper, and analyzed. Free iodine was determined by titration, and potassium iodide by heating to remove free iodine and benzene. Benzene was determined by difference.

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[1] Abegg and Hamburger: Z. anorg. Chem., 50, 403 (1905).

TABLE I

System: C_6H_6–KI–I_2

Showing the solubility at the two univariant points at each temperature and the molecular ratio of free iodine to potassium iodide in the residues

Temperature, 25°		Temperature, 6°	
% I_2 in Solution	Molecular Ratio, I_2 : KI, in Solid	% I_2 in Solution	Molecular Ratio, I_2 : KI, in Solid
9.07	.03	4.77	0.26
9.16	.04	4.65	2.42
8.99	.34	4.69	2.90
9.07	.83	4.65	3.31
9.15	1.20	4.64	3.56
9.03	1.89		
9.09	2.26	8.54	4.46
9.12	2.45	8.60	11.95
9.08	2.62		
9.12	2.79		
9.11	3.34		
9.12	3.65		
8.99	3.74		
14.22	4.27		
14.19	4.90		
14.18	8.45		

We give below, in Table II, the results obtained on every residue analyzed, including one which was allowed to stand too long in the air and had begun to lose benzene.

TABLE II

Showing the composition of the solutions with which the ternary compound is in equilibrium, and the analyses of the compound

	% I_2 in Solution	Analyses of Compound		
		% KI	% I_2	% C_6H_6
		Temperature, 6°		
1	5.26	11.65	71.82	16.53
2	5.80	11.81	70.98	17.21
3	6.13	11.56	71.17	17.27
4*	6.30	12.46	75.70	11.84
5	6.76	12.13	71.81	16.06
6	7.53	11.38	71.45	17.17
		Temperature, 25°		
7	10.69	11.80	70.83	17.37
8	12.14	11.42	70.96	17.62
9	13.31	11.59	70.20	18.21
Average (excluding No. 4)		11.67	71.15	17.18
Calculated for KI·4I_2·3C_6H_6 =		11.73	71.72	16.55
Calculated for KI·3I_2·2C_6H_6 =		15.32	70.27	14.41

*The solid had begun to lose benzene before analysis. Ratio of KI to I_2 is 1:3.97.

The results of the analyses lead to the formula $KI \cdot 4I_2 \cdot 3C_6H_6$ rather than to the formula $KI \cdot 3I_2 \cdot 2C_6H_6$ proposed by Grace.

The analytical results on the compound can be checked indirectly since the weights of the three components were accurately known in all experiments. By assuming the composition of the addition product, the composition of the solution can thus be readily calculated and compared with the composition found by analysis. In Table III we give the weights of each component in the original mixtures, the calculated per cent of iodine in solution assuming (a) the formula proposed by Grace and (b) the formula which we have proposed. The per cent of iodine found by analysis is in the last column.

TABLE III

Showing the weight of each component in the original mixtures, the calculated per cent of iodine in solution assuming (a) the solid has the formula $KI \cdot 3I_2 \cdot 2C_6H_6$ proposed by Grace, (b) the solid has the formula $KI \cdot 4I_2 \cdot 3C_6H_6$. The per cent of iodine found by analysis is given in the last column.

KI gms.	I_2 gms.	C_6H_6 gms.	Calculated % I_2 in Solution (a)	Calculated % I_2 in Solution (b)	% I_2 in Solution (Analysis)
			Temperature, 6°		
0.429	4.069	29.756	6.68	4.73	5.26
0.704	6.043	30.193	8.70	5.62	5.80
0.429	4.396	29.984	7.59	5.69	6.13
0.82	6.87	29.937	9.63	6.05	6.30
0.704	6.36	30.014	9.64	6.61	6.76
0.82	7.29	29.980	10.78	7.32	7.53
			Temperature, 25°		
0.82	8.39	30.145	13.62	10.43	10.69
0.82	8.86	29.625	15.02	11.90	12.14
0.82	9.33	29.861	16.07	13.07	13.31

It will be noticed that the solubilities calculated by assuming that the residue is $KI \cdot 4I_2 \cdot 3C_6H_6$ agree rather closely with the solubilities determined, while if the residue is assumed to be $KI \cdot 3I_2 \cdot 2C_6H_6$ (Grace formula) the calculated solubility is very different from the results of analysis. It would appear, therefore, from the data on the univariant systems (Table I), from the analyses of the pure compound (Table II), and from the calculated solubilities (Table III) that the ratio of $KI : I_2$ is $1:4$. The only reliable data on the molecular ratio of benzene is contained in Table II, but the results of eight of the nine analyses show three molecules of benzene to be present and in the one exceptional case (No. 4) the salt clearly showed by its appearance that it had begun to decompose.

In concluding, it seems well to point out that these results are not in disagreement with the results found by Grace using water as a solvent. He found, as did Foote and Chalker[1] much earlier, that there were three univariant points in the water system, with two corresponding addition products in which the ratio of KI to I_2 is $1:1$ and $1:3$, respectively. It is evident, however, that these compounds must be hydrated, since no binary addition product exists, and Grace assigned the formulas $KI_3 \cdot H_2O$ and $KI_7 \cdot H_2O$. The small percentage of water in these compounds escaped detection in the earlier work. Bancroft, Scherer and Gould appear not to have considered the possibility of hydrate formation in their discussion.

Summary

1. The solubility results on mixtures of potassium iodide and iodine with chloroform and with toluene show that between $25°$ and $0.7°$, no solid binary addition product of potassium iodide and iodine exists.

2. With benzene, a ternary addition product exists, having the formula $KI \cdot 4I_2 \cdot 3C_6H_6$.

3. These results are not in disagreement with the results of Grace on the ternary system with water, who showed, as have others, that there are two addition products in which the ratio of KI to I_2 is, respectively, $1:1$ and $1:3$. These, however, must be ternary hydrated compounds, as Grace pointed out.

New Haven, Connecticut.

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[1] Foote and Chalker: Am. Chem. J., **39**, 561 (1908).

THE INFLUENCE OF TEMPERATURE ON THE OXIDATION POTENTIALS OF MIXTURES OF FERRIC AND FERROUS CHLORIDES IN HYDROCHLORIC ACID SOLUTION

BY SYDNEY RAYMOND CARTER AND THOMAS JOSEPH GLOVER

It has been shown by Carter and Clews[1] that the oxidation-reduction potentials of mixtures of ferric and ferrous chlorides in hydrochloric acid are so modified by the acid that its presence would probably account for the anomalies observed by Wardlaw and Clews[2] in the oxidising and reducing reactions of these mixtures in hydrochloric acid with sulphur dioxide. In order, however, to institute a closer comparison between the sulphur dioxide observations which were made at 100°C and the potential measurements, which were taken at room temperature, it was necessary to determine how the latter values would be affected by change in temperature. For this object the following investigation was undertaken.

Experimental

Preparation of solutions. The ferrous chloride solutions were prepared from pure iron and hydrochloric acid, whilst those of ferric chloride were obtained by dissolving the anhydrous solid in this acid. The solutions were made up as nearly as possible to the composition required and the actual composition then determined by analysis.

The ferric iron was estimated by reduction with titanous chloride using an excess of potassium thiocyanate as an indicator.[3] The total iron was determined by oxidising the ferrous chloride present with sodium peroxide and titrating as before with titanous chloride. The ferrous iron was then obtained by difference. The total chlorides were estimated as silver chloride and the free hydrochloric acid calculated.

Apparatus. The oxidation half element, which was furnished with four recently platinised platinum electrodes, consisted of a glass vessel containing about 100 ccs. of the acid ferrous-ferric chloride solution over which was enclosed an atmosphere of carbon dioxide. The solution was connected with a normal calomel electrode by a chain of three intermediate vessels, the one next the calomel electrode containing normal potassium chloride and the other two the same solution as the oxidation half element. The connecting syphons had tubes attached resembling handles to tuning forks. The syphons were filled and any bubbles which collected during the progress of the experiment were removed by suction through these tubes which were afterwards closed with glass plugs. In order to keep down the electrical resistance of the

[1] Knecht and Hibbert: "New Reduction Methods in Volumetric Analysis."
[1] J. Chem. Soc., **125**, 1880 (1924).
[3] J. Chem. Soc., **117**, 1093 (1920).

cell the syphon tubes were of wide bore (*ca.* 7 mm.)   The limbs of the syphon connecting the normal potassium chloride vessel with the ferrous-ferric vessel next to it, were made about five inches apart to permit of the two parts of the cell being placed in two different thermostats simultaneously when so required.   This syphon was fitted with a tap which was open only whilst potential readings were being taken.

Potential Measurements.   The cell was allowed to stand in the 20°C thermostat for about half an hour, after which, the e.m.f. was observed about every five minutes until a constant value was attained.   If any one of the platinum electrodes continued to disagree appreciably from the others it was replaced by a new one.   A Tinsley potentiometer and galvanometer were used to measure the potentials, observations of which were taken to the nearest tenth of a millivolt.   Constant e.m.f. readings were as a rule easy to obtain except when the cell appeared to have become polarised.

The e.m.f. having been measured at 20°C the cell was transferred to the 60°C thermostat and the e.m.f. measured in the same way as at the lower temperature.   Finally the calomel electrode and adjacent vessel were placed in the thermostat at 20°C whilst the oxidation half element and the other two vessels were allowed to remain in the 60°C thermostat.   The e.m.f. of the cell as thus arranged was again measured.

The concentrations of the ferrous and ferric iron are denoted by $[Fe^{II}]$ and $[Fe^{III}]$ respectively and they refer to salt concentrations.   The e.m.f.'s of the oxidation cells at 20°C, 60°C and 20°C-60°C as above described, are denoted by E_b, E_d, and E_f respectively.

The Influence of Temperature on the E.M.F. of the Oxidation Cells.   Table I gives the potentials of a number of cells in which the hydrochloric acid of the oxidation half element is at varying concentrations.   Slight corrections are applied to the observed e.m.f.'s to bring the acid concentrations to the rounded values given in Table I, and they are tabulated in columns 3 and 4 for the temperatures 20°C and 60°C respectively.   It will be seen that for any given acid concentration the potential increment for this temperature interval, increases with a rise in percentage of ferric salt, which is in accordance with the logarithmic formula stated below.   It will be also observed that for a ferrous-ferric mixture of given proportion the potential rise due to the increase of temperature falls off with diminishing acid concentration.

Variation of Potential at 20°C and 60°C with Proportion of Ferric Iron.   The potentials when $[Fe^{II}] = [Fe^{III}]$, which are denoted by E_o have been calculated by the formula

$$E_0 = E + RT/nF.\log [Fe^{II}]/[Fe^{III}] = E + 0.0001983\, T \log [Fe^{II}]/[Fe^{III}].$$

The numerical value of the factor RT/nF has been taken as $0.0001983T$ or 0.0581 and 0.0661 for 20°C and 60°C respectively, and the constancy of the potential E_o in columns 5 and 6, Table I shows that the logarithmic formula holds at both temperatures for the acid concentrations stated when the values of the ferric and ferrous salt concentrations are substituted in this formula. Previous work[1] had only verified this relation for a lower temperature 17°C.

[1] J. Chem. Soc., **124**, 1881 (1924).

TABLE I

Solution No.	$\dfrac{[Fe^{III}] \times 100}{[Fe^{II}] + [Fe^{III}]}$	E_b t = 20°C	E_d t = 60°C	E_{bo} t = 20°C	E_{do} t = 60°C
		[HCl] = 0.100 N			
1	25.78	0.4056	0.4355	0.4323	0.4657
2	50.66	0.4339	0.4652	0.4332	0.4645
		[HCl] = 1.000 N			
3	6.34	0.3219	0.3294	0.3899	0.4067
4	26.42	0.3640	0.3808	0.3899	0.4102
5	50.00	0.3923	0.4118	0.3923	0.4118
6	74.49	0.4179	0.4417	0.3909	0.4109
		[HCl] = 3.00 N			
7	15.79	0.3037	0.3022	0.3459	0.3503
8	50.78	0.3481	0.3528	0.3473	0.3519
9	75.33	0.3783	0.3876	0.3499	0.3553
10	87.62	0.3971	0.4055	0.3477	0.3494
		[HCl] = 4.90 N			
11	21.03	0.2724	0.2651	0.3058	0.3030
12	42.27	0.2958	0.2926	0.3037	0.3026
13	52.06	0.3090	0.3084	0.3068	0.3060
14	64.71	0.3203	0.3206	0.3050	0.3033
15	68.11	0.3272	0.3285	0.3081	0.3068
16	77.50	0.3368	0.3387	0.3056	0.3032
		[HCl] = 6.66 N			
17	28.92	0.2409	0.2313	0.2636	0.2571
18	44.96	0.2557	0.2473	0.2608	0.2531
19	52.43	0.2679	0.2572	0.2654	0.2544
20	78.29	0.2977	0.2934	0.2653	0.2566
		[HCl] = 10.02 N			
21	40.84	0.1777	0.1757	0.1871	0.1681
22	57.59	0.1912	0.1733	0.1836	0.1645
23	80.54	0.2219	0.2075	0.1861	0.1667
1	2	3	4	5	6

The Diffusion Potential for junctions of the Type xN HCl — N KCl. Dilute Acid. In the case of 0.1 N and 1 N HCl the contact potentials were calculated by Henderson's formula which for junctions of two binary electrolytes containing only monovalent radicles simplifies[1] to the relation

$$\pi = \frac{RT}{F} \cdot \frac{C_1(u_1 - v_1) - C_2(u_2 - v_2)}{C_1(u_1 + u_1) - C_2(u_2 + v_2)} \log \frac{C_1(u_1 + v_1)}{C_2(u_2 + v_2)}$$

[1] Cumming: Trans. Faraday Soc., **8**, 86 (1912).

The potentials found thus for the above junctions amounted to 0.0096 and 0.0276 volt at 20°C and 0.0077 and 0.0254 at 60°C respectively.

The ionic mobilities at infinite dilution, H = 327, Cl = 68, K = 67 at 20°C and H = 505, Cl = 134, K = 133 at 60° were derived from data given in the Smithsonian Tables.[1]

Concentrated Acid.

The contact potentials for junctions involving concentrated acids were obtained by measuring the e.m.f.'s of the cells set out below. The potential (0.028 volt) for the junction N HCl − N KCl was calculated by using Henderson's[2] formula whilst the values 0.0505 and 0.0806 for the contact potentials at the junctions 4.9 N HCl − N HCl and 10 N HCl − N HCl respectively were obtained from measurements by Carter and Lea.[3] The directions of the potentials are indicated by arrow heads and are considered as operating within the cell.

Hg	Hg$_2$Cl$_2$ 4.9 N HCl	4.9 N HCl	N KCl $\rightarrow$ π	Hg$_2$Cl$_2$ N KCl	Hg

$$E = 0.1483$$

Hg	Hg$_2$Cl$_2$ 4.9 N HCl	4.9 N HCl $\rightarrow$ 0.0505	N HCl $\rightarrow$ 0.028	N KCl	Hg$_2$Cl$_2$ N KCl	Hg
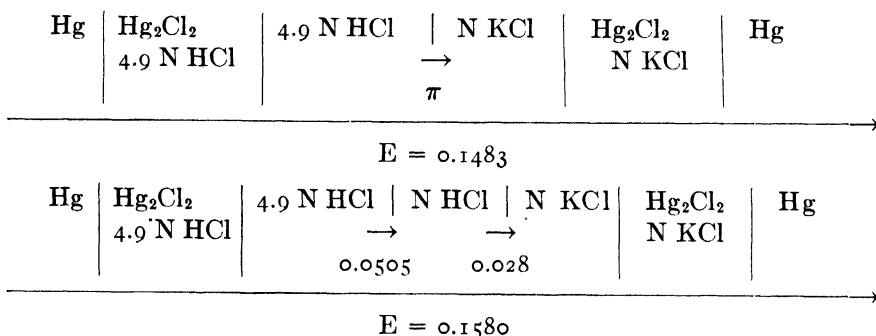
$$E = 0.1580$$

The e.m.f.'s of the complete cells were found to be 0.1483 and 0.1580 respectively whence π = 0.0688 volt.

For cells containing 10.0 N HCl the corresponding values were 0.2461 and 0.2598 which gives π = 0.0950 volt.

The four values of the contact potential thus obtained by the two methods were plotted against acid concentration and these together with two further values for 3 N and 6.66 N HCl obtained by extrapolation are tabulated in Column 8, Table II.

Variation of the Diffusion Potentials with Temperature.

The values obtained by Henderson's formula as given above for the 0.1 N HCl − N KCl and N HCl − N KCl contact potentials diminish with temperature but only by a small amount.[4]

If either of the solutions concerned is concentrated, Henderson's formula is no longer valid for calculating contact potentials.

[1] Johnson: J. Am. Chem. Soc., **31**, 1010, (1909).
[2] Loc. cit.
[3] J. Chem. Soc., **127**, 487 (1925).
[4] cf. Prideaux: Trans. Faraday Soc., **44**, 11 (1928). *

Accurate determinations of the temperature coefficient of the diffusion potentials were not made but values of this coefficient which should be of the correct order of magnitude and would therefore be approximate enough for the main purposes of this investigation were obtained in the following way.

TABLE II

[HCl]	E_{do}	E_{fo}	Temperature coefficient $\times 10^4$					
			Calomel Electrode					
			'Apparent'		'True'			
			obs	graph		$\triangle\pi/\triangle t$	π_{20}°	π_{60}°
0.0	0.4770	0.5014	6.1	6.1	6.1	0.0	0.0000	0.0000
0.1	0.4651	0.4867	5.4	5.5	6.1	−0.6 (1)	0.0096	0.0072(1)
						−0.52(2)		0.0077(2)
1.0	0.4099	0.4302	5.07	5.1	6.1	−1.0 (1)	0.0276	0.0236(1)
						−0.55(2)		0.0254(2)
3.0	0.3517	0.3715	4.95	4.8	6.1	−1.3	0.0505	0.0453
4.9	0.3041	0.3219	4.44	4.7	6.1	−1.4	0.0688	0.0632
6.66	0.2553	0.2763	(5.25)	4.65	6.1	−1.45	0.0785	0.0727
10.02	0.1664	0.1844	4.50	4.50	6.1	−1.6	0.0949	0.0885
1	2	3	4	5	6	7	8	9

The variation with temperature of contact potential at xN HCl − N KCl junctions can be approximately computed from the difference between the 'true' and 'apparent' temperature coefficient of the calomel electrode. When the cell is arranged as described for the measurement of E_f the xN HCl − N KCl junction would normally be situated in the syphon between the 20°C and 60°C thermostats and its temperature is assumed to be 20°C whilst for the arrangement when both the cell and calomel electrode are in the 60°C thermostats the junction is assumed to be at 60°C.

The 'apparent' temperature coefficient of the calomel electrode is given by $(E_{fo} − E_{do})/(t_{60} − t_{20})$ and the 'true' temperature coefficient is taken as 0.00061 as found by Richards[1]. The temperature coefficient of diffusion potential is thus given by the expression

$$\triangle\pi/\triangle t = (E_{fo} − E_{do})/(t_{60} − t_{20}) + 0.00061$$

The experimentally determined 'apparent' calomel electrode temperature coefficients (Column 3 Table II) were plotted against the HCl concentration at the liquid junction and the smoothed values (Column 5) were used in the calculations.

Referring to Table II, column 2 gives mean values of E_{do} taken from Table I Column 5, and Column 3 Table II gives the result of a series of potential measurements of the oxidation cells when arranged as described to measure E_{fo}. In each case they are the means of the observed values for the condition $[Fe^{III}] = [Fe^{II}]$. The values given for [HCl] = 0.0 here and elsewhere in this paper have been obtained by extrapolation.

[1] Z. physik. Chem., 24, 39 (1897).

Alternative values are given in Columns 7 and 9 Table II for 0.1 N HCl and 1.0 N HCl, the first (1) being calculated from e.m.f. observations as described above and the second (2) from Henderson's formula. In subsequent calculations only values (1) have been used.

Variation with Temperature of the Potential of the Oxidation Half Element.

Referring to Table III columns 1 and 2 give mean values for E_{bo} and E_{do} taken from columns 5 and 6 Table I. The temperature coefficients of the whole cell $(E_{do} - E_{bo})/(t_{60} - t_{20})$, of the contact potential and of the calomel electrode are given in columns 4, 5 and 6 respectively. The sum of these three values furnishes the temperature coefficients of the oxidation half element tabulated in column 7.

TABLE III

			$\triangle E/\triangle t \times 10^4$			
[HCl]	E_{bo} t = 20°C	E_{do} t = 60°C	Whole Cell	Contact Potential	Calomel Electrode	Oxid. half Element
0.00	0.4430	0.4770	+8.50	0.00	6.1	+14.60
0.10	0.4328	0.4651	+8.07	−0.60	6.1	+13.57
1.00	0.3907	0.4099	+4.80	−1.00	6.1	+ 9.90
3.00	0.3477	0.3517	+1.0	−1.30	6.1	+ 5.80
4.90	0.3058	0.3041	−0.42	−1.40	6.1	+ 4.28
6.66	0.2638	0.2553	−2.12	−1.45	6.1	+ 2.53
10.02	0.1856	0.1664	−4.80	−1.60	6.1	− 0.30
1	2	3	4	5	6	.7

Heats of Reaction derived from Potential-Temperature Measurements.

The reaction occurring in the oxidation cell should give a heat of reaction U which can be calculated by the aid of the Gibbs-Helmholtz equation $U = EnF - TnF \cdot dE/dT$, where E refers to the e.m.f. of the cell from which the contact potential has been eliminated. The heats of reaction calculated by this equation are given in Table IV column 4. The contact potentials operating in the cell were taken from Table II columns 8 and 9 and as they act in opposition to the main potential of the cell the values of E given in columns 2 and 3 Table IV were obtained by adding them to the observed e.m.f.'s of the cell.

TABLE IV

[HCl]	$E = E_{bo} + \pi_{20}$	$E = E_{do} + \pi_{60}$	U Cals.
0.0	0.4430	0.4770	4.49
0.1	0.4424	0.4723	5.16
1.0	0.4183	0.4335	7.09
3.0	0.3982	0.3970	9.38
4.9	0.3746	0.3673	9.87
6.66	0.3423	0.3280	10.30
10.02	0.2805	0.2549	10.78
1	2	3	4

At zero concentration of acid the reaction in the cell will be due to

$$Fe^{+++} + Hg \text{ (metal)} + Cl^- = Fe^{++} + HgCl$$
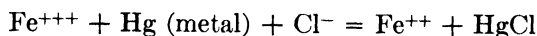
for which U = 4.49 Cals.

It will be seen that a rise in the concentration of acid is accompanied by an increase in the value of U. This increase is decidedly rapid up to a moderate concentration of *ca* 3 N after which it is less pronounced. The reason for this is not clear and an explanation is reserved until later.

Evaluation of Equilibrium Constant for the Cell Reaction.

At zero acid concentration the reaction would not be complicated by the presence of acid and the contact potential would vanish since the diffusion potential due to the iron salts and the N KCl is neglected and the contact potential is eliminated by the extrapolation. The equilibrium constant K can then be calculated by the equation, $E_o = RT/nF \cdot \log K$. Using the E_o values for zero acid concentration given in Table IV, 0.4430 and 0.4770 volts at 20°C and 60°C respectively, the values obtained for K are $10^{7.624}$ and $10^{7.228}$ at 20°C and 60°C respectively.[1]

Heat of Reaction from Isochore Equation.

By substituting the values given above for K in the Reaction Isochore equation $\log K_1 - \log K_2 = U/R \cdot (1/T_1 - 1/T_2)$ the value obtained for the heat of reaction U is 4.43 Calories which result agrees with that found using the Gibbs-Helmholtz equation and given for zero acid concentration in Table IV.

The Influence of Temperature on the Oxidation Potentials of mixtures of Ferrous and Ferric Chlorides in Hydrochloric Acid viewed in relation to the action of Sulphur Dioxide on these mixtures.

In Tables V and VI are given the increment in potential due to a rise in temperature from 20°C to 100°C. Table V refers to mixtures where $[Fe^{III}] = [Fe^{II}]$, and Table VI refers to two mixtures in one of which $[Fe^{III}]/[Fe^{II}] = 99.5/0.5$ and in the other $[Fe^{III}]/[Fe^{II}] = 0.5/99.5$. The potentials of the liquid junction and the calomel electrode being opposite in sign to that of the cell are added to the cell e.m.f. to obtain the potential of the oxidation half element. Thus the values for the potentials of the oxidation half element, denoted by E_e are obtained by adding to the E_o values given in Table III columns 2 and 3 the appropriate contact potential and the potential of the calomel electrode (0.5612 volts at 20°C.) The values for E_e at 100°C are calculated from E_e at 20°C by means of the temperature coefficients given in Table III column 7. The values for E_e when $[Fe^{III}]$ is not equal to $[Fe^{II}]$, and given in Table VI, are obtained by adding to the corresponding E_e values in Table V the appropriate value of $RT/nF \cdot \log [Fe^{III}]/[Fe^{II}]$.

[1] Cf. Peters: Z. physik. Chem., **26**, 193 (1895).

TABLE V

[HCl]	E_e t = 20°C	E_e t = 100°C	$\triangle E_e$
0.0	1.0042	1.1210	+0.1168
0.1	1.0037	1.1122	+0.1085
1.0	0.9795	1.0587	+0.0792
3.0	0.9594	1.0058	+0.0464
4.9	0.9358	0.9700	+0.0342
6.66	0.9035	0.9237	+0.0202
10.02	0.8417	0.8393	−0.0024

TABLE VI

[HCl]	[Fe^{III}]/[Fe^{II}] = 99.5/0.5			[Fe^{III}]/[Fe^{II}] = 0.5/99.5		
	E_e t = 20°C	E_e t = 100°C	$\triangle E_e$	E_e t = 20°C	E_e t = 100°C	$\triangle E_e$
0.0	1.1376	1.2912	0.1536	0.8706	0.9508	+0.0802
0.1	1.1373	1.2824	0.1451	0.8701	0.9420	+0.0719
1.0	1.1131	1.2289	0.1158	0.8459	0.8885	+0.0426
3.0	1.0930	1.1760	0.0830	0.8258	0.8356	+0.0098
4.9	1.0694	1.1402	0.0708	0.8022	0.7998	+0.0024
6.66	1.0371	1.0939	0.0568	0.7699	0.7535	−0.0164
10.02	0.9753	1.0095	0.0342	0.7081	0.6691	−0.0390

A general idea of the influence of temperature on the oxidation potentials of ferric and ferrous chlorides in hydrochloric acid of varying concentration may be gained from Tables V and VI. From the values of the increments in potential E_e due to a rise in temperature from 20°C to 100°C the following conclusions may be deduced.

1. The increment in potential with temperature diminishes with increasing acid concentration.

2. Mixtures containing a much larger proportion of ferric than ferrous chloride have their potentials raised by temperature at all acid concentrations.

3. In mixtures containing a high proportion of ferrous chloride the effect of temperature is to raise the potential in low acid concentrations but to depress it in solutions of high acid concentration.

The general inference is that at the higher temperature ferric chloride is a better oxidising agent whilst ferrous chloride is a better reducing agent. Hence either ferrous chloride or ferric chloride would react rather more readily with sulphur dioxide at the higher temperature than might have been supposed from potential measurements taken at the room temperature. Tables V and VI also show that the effect of temperature on these oxidation potentials is of a small order compared with those produced by changes in acid concentration, and hence the previous interpretations[1] of the sulphur dioxide quantitative experiments of Wardlaw and Clews,[2] based on potential measurements at room temperature were not affected by neglect of temperature.

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[1] J. Chem. Soc., **124**, 1885 (1924).

[2] Loc. cit.

Summary

1.   The potentials of cells in which the oxidation half element consisted of mixtures of ferric and ferrous chlorides in hydrochloric acid varying in concentration from 0.1 N to 10.02 N have been measured at 20°C and 60°C.

2.   A logarithmic relation between the e.m.f. of the oxidation cell and the ratio of ferric to ferrous iron has been shown to hold at both temperatures.

3.   The heat of the cell reaction has been calculated for various concentrations of hydrochloric acid.

4.   Approximate values have been obtained for the potential increment of the oxidation electrode with rise in temperature and the significance of these potential increments has been discussed in their relation to (a) the oxidising and reducing properties of ferric and ferrous chloride, and (b) the action of sulphur dioxide on these mixtures in weak and concentrated hydrochloric acid.

A STUDY OF ORGANIC-ACID IRON SOLUTIONS*

III. Complex-Colloid Equilibrium

BY NORMAN J. HARRAR AND FRANK E. E. GERMANN

Introduction

In a previous paper,[1] the purpose and plan of this work were explained in detail. Quantities of freshly precipitated ferric hydroxide were dissolved in various organic acids and concentrations of about one gram of iron in 250 cc. of one normal acid solutions were obtained. Standard methods of analysis were used to find the exact amounts of iron and of acid present in each case. The colors of the solutions, the colors on dilution and the relative color intensities were determined for each combination. It was found that an arrangement of the acids tested, in the order of their dissociation constant values, would show a definite division into two groups—strong acids with green colored solutions—weak acids with red colored solutions.

In a second paper,[2] the results obtained from experiments involving dialysis, reflection of light and diffusion were described in detail. Further support was provided for the generalization that the most important factor in determining the properties of these substances is the strength of the acid involved. Many similarities were observed between the properties of a colloidal ferric hydroxide and those of the weak acid preparations, but even these appeared to contain some iron in true solution. It seemed probable that a satisfactory explanation of the facts must assume that some sort of an equilibrium exists between several different complex forms. This idea will be developed further in the sequel.

Electrolysis

The determination of the chemical formula and the structure of the more common of these complexes, such as the acetate and the oxalate, has been the object of many investigations. It has been shown that the iron of the acetate is in a complex red cation and that the iron of the oxalate is in a complex green anion. A type of experiment was devised, therefore, to check the statements regarding the familiar complexes and to extend the comparison to cover all these preparations.

For this purpose, an ordinary U-tube was filled with a portion of solution, two platinum electrodes inserted and a direct current applied for some time. The movement of the iron in the tube was ascertained by several methods. With the intensely colored red solutions, actual shifts of color could be observed. With the more weakly colored preparations, however, it was neces-

sary to withdraw small portions from each side of the tube and test them with NH₄CNS solution. In making this test, concentrated HCl was added to break up the iron complex and permanganate was added to oxidize any ferrous iron formed during the electrolysis.

The results obtained with those combinations to which this method could be satisfactorily applied are given in Table IX.

TABLE IX

Positive Complexes	Negative Complexes	Evidence for Both Types
Acetic	Oxalic	Formic
Propionic	Malonic	
Butyric		Maleic
Succinic		Dichloracetic
Glutaric		
Adipic		

The results of these experiments are in accord with those obtained from the other methods of comparison. As in the dialysis tests, the formate solution presented the most unusual features in its electrolysis. There was a movement of the red color towards the cathode, as with the acetate and propionate, but an analysis did not show more iron on that side. Furthermore, the solution around the anode became colorless or developed a trace of green color.

It will be recalled that the dialysis of the formate solution gave a green color, at first, outside the cup. Some of this pale green dialysate, therefore, was placed in a tube and subjected to electrolysis, and a definite increase in iron on the anode side was observed. These facts give further support to the suggestion already advanced, that in the formate solution, both positive and negative, red and green, complexes are present.

The results obtained with the maleic and dichloracetic acid combinations make it appear that both types of complexes exist in these solutions also. All the evidence of the other methods of comparison is in agreement with this conclusion.

Stronger Concentrations

The color changes produced when solutions of these iron complexes were diluted have already been described. In view of the fact that the idea of an equilibrium between complex forms is being developed, it is also important to know the effect of increasing the acid concentrations. Since the first three acids on the list, formic, acetic, and propionic, are liquids, perfectly miscible with water, it was most convenient to use them for experiments of this kind.

It was of prime importance to determine the effect of a greater acid concentration upon the formate. The evidence already accumulated indicates that this complex occupies an intermediate position between the conditions in which red cations or green anions predominate. It should show most readily, therefore, the effects resulting from changes in the acidity of its solutions.

A further incentive to this kind of study of the formate complex is provided by the following statement from the work of Weinland and Reihlen:[3] "By the addition of solid sodium formate to such a solution, the red color gradually becomes pale, and tri sodium hexaformato-ferrate $(Fe(HCO_2)_6)Na_3$ separates in pale green, microscopic, rectangular tablets." It seemed probable that increasing the formic acid concentrations in the preparations under investigation would have somewhat the same general effect.

The tests were carried out with the formate, acetate, and propionate preparations, using the row of bottles produced by diluting the original normal solutions. Starting with the most dilute (bottles 12 and 11), quantities of the pure acid were added until the yellow color was removed. With the acetate and propionate solutions the color could be removed only from two or three bottles (numbers 12, 11, 10), although a more reddish tint was developed in the higher concentrations.

With the formate solutions the color could be removed in all the bottles up to number 3, and weakened somewhat in the remaining ones. Here again, it seems that the superior strength of the formic acid can cause a reversal of the red complex, while the weak acids cannot accomplish such a change.

Formulas of the Complexes

Some of the general conclusions reached as a result of this work are based partly upon the accepted formulas of the more familiar of these compounds. It is necessary, therefore, to list the formulas suggested for those substances which have been investigated.

It is beyond the scope of this article to describe or explain the methods used in determining the exact formulas proposed for these complexes. However, it may be indicated that, in general, double decomposition reactions between ferric chloride and salts of organic acids have been made to yield crystalline compounds, which are submitted to an anaylsis. On the other hand, much of the information regarding their composition has been obtained by rather indirect methods.

A review of the literature and suggestions about formulas have been condensed into Table X. The largest contributions have been made by R. F. Weinland and his co-workers and most of the formulas given in the table are taken from his publications. Since the present series of articles was begun, the research of W. D. Treadwell and W. Fisch[4] has been published and contains information of great value

The formulas of the complex oxalate and malonate seem to have been accepted years ago and there is some doubt as to whom credit is due for recognizing their precise nature. There are other cases in which it is probable that the constitution was understood, but reference is made only upon the basis of the proposal of an actual formula.

[3] Ber., **46**, 3148 (1913).

[4] Treadwell and Fisch: Helv. Chim. Acta, **13**, 1223 (1930).

TABLE X

Acids	Formulas of Complexes	Important Contributions
Formic	$[Fe_3(HCO_2)_6]^{+++}$	E. Ludwig: Archiv. Pharm., **107**, 1 (1861).
	$[Fe_3(HCO_2)_6(OH)_2]^+$ $[Fe(HCO_2)_6]^\equiv$	Scheurer and Kestner: Bull., **1863**, 346; E. Belloni: Archiv. Pharm., **247**, 123 (1909); Weinland and Reihlen: Ber **46**, 3148 (1913); O. F. Tower: J. Am. Chem. Soc., **32**, 956 (1910); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1222 (1930).
Acetic	$[Fe_3(C_2H_3O_2)_6(OH)]^{++}$	E. Mayer: Jahr. Fort. Chem., **9**, 487 (1856);
	$[Fe_3(C_2H_3O_2)_6(OH)_2]^+$	A. Bettendorff: Z. Chem.,**1866**,645; Weinland and Gussman: Ber., **42**, 3881 (1909); P. S. U. Pickering: J. Chem. Soc., **105 I**, 464 (1914); N. Lofman: Z. anorg. Chem., **107**, 257 (1919); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1209 (1930).
Propionic	$[Fe_3(C_3H_5O_2)_6(OH)_2]^+$	A. Benrath: J. prakt. Chem., (2) **72**, 232 (1875).
Butyric	$[Fe_3(C_4H_7O_2)_6(OH)_2]^+$	Treadwell and Fisch: Helv. Chim. Acta, **13**, 1223 (1930).
Oxalic	$[Fe(C_2O_4)_3]^\equiv$	J. Bussy: J. prakt. Chem., **16**, 399 (1839); Eder and Valenta: Monatshefte, **1**, 763 (1880); H. Schafer: Z. anorg. Chem., **45**, 293 (1905); Cameron and Robinson: J. Phys. Chem., **13**, 157 (1909); W. Thomas: J. Chem. Soc., **119**, 1140 (1921); Weinland and Loebich: Z. anorg. Chem., **151**, 271 (1926); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1225 (1930).
Malonic	$[Fe(C_3H_2O)_4]^\equiv$	A. Scholtz: Monatshefte, **29**, 444 (1908); Jaeger and Mees: Proc. Acad. Sci., Amsterdam, **20**, 283 (1917);

<div align="center">TABLE X (Continued)</div>

Acids	Formulas of Complexes	Important Contributions
Malonic	$[Fe(C_3H_2O)_4]^{\equiv}$	Weinland and Loebich: Z. anorg. Chem., **151**, 271 (1926); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1226 (1930).
Succinic	$[Fe_3(C_4H_4O_4)_3(OH)_2]^{++}$	O. Doepping: Ann., **47**, 279 (1843); A. Handl: Jahr. Fort. Chem., **12**, 279 (1859); Weinland and Paschen: Z. anorg. Chem., **92**, 116 (1915); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1226 (1930).
Glutaric		A. Scholtz: Monatshefte, **29**, 446 (1908).
Adipic		
Tricarballylic		
Maleic		A. Scholtz: Monatshefte, **29**, 444 (1908); Weinland and Paschen: Z. anorg. Chem., **92**, 116 (1915).
Fumaric	$[Fe_3(C_4H_2O_4)_2(OH)_3]^{++}$ and others	S. Rieckher: Ann., **49**, 55 (1844). Weinland and Paschen: Z. anorg. Chem., **92**, 116 (1915); A. Scholtz: Monatshefte, **29**, 444 (1908).
Mesaconic		
Chloracetic	$[Fe_3(ClC_2H_2O_2)_6(OH)_2]^+$ and others	A. Benrath: J. prakt. Chem., (2), **72**, 231 (1875); Weinland and Loebich: Z. anorg. Chem., **151**, 273 (1926); Treadwell and Fisch: Helv. Chim. Acta, **13**, 1223 (1930).
Dichloracetic		
Trichloracetic	$[Fe_3(Cl_3C_2O_2)_6(OH)_2]^+$ and others	F. M. Jaeger: Chem. Zentr., **82**, II 1851 (1911); **83**, I 1817 (1912). Weinland and Loebich: Z. anorg. Chem., **151**, 274 (1926).
Benzoic	$[Fe_3(C_6H_5CO_2)_6(OH)_2]^+$ and others	R. F. Weinland: "Einfuhrung in die Chemie der Komplex-Verbindungen" (1919). Weinland and Herz: Ber., **45**, 2662 (1912).
Phenylacetic		
Phthalic	$[Fe(C_6H_4C_2O_4)_3]^{+++}$ and others	Weinland and Paschen: Z. anorg. Chem., **92**, 92 (1915).

Conclusions

It is neither convenient nor absolutely necessary to review, at this point, all the implications of the data collected in this study. The descriptions of experimental work and the tabulations of results have been followed by detailed discussions. During this presentation, two general conclusions have been advanced and tested repeatedly, until they seem to have been rather definitely established.

1. The most important factor in determining the properties of these organic iron complexes is the strength of the acid involved.

2. Solutions of these substances may contain more than one complex form at the same time.

If it may be assumed that these statements are valid, in the light of the work as a whole, it is possible to combine them into a third significant conclusion.

3. Equilibrium conditions exist between the various complex forms and are controlled, primarily, by the acidity of the solution.

Upon this basis, a careful study has been made of the formulas proposed for some of these complexes and of the comparative data collected in the present work. An outline of the recognized forms of these substances and of their relationships is given in the following diagram. The formulas are merely type examples, derived from the compilation in Table X, but the arrangement reflects the attempt of this work to determine the conditions under which the various forms exist.

TABLE XI
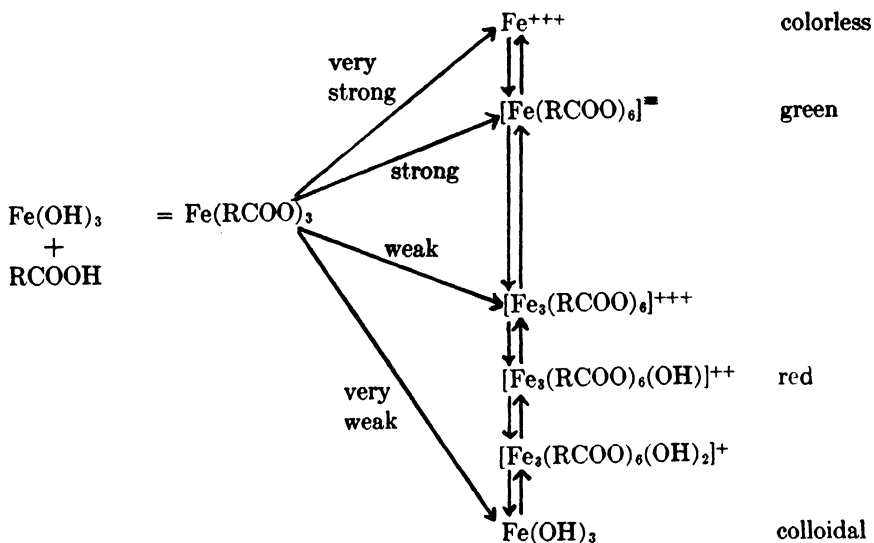
This scheme indicates exactly, for the first time perhaps, what is believed to be the influence of acid strength upon the color and structure of these complex forms. These conclusions are really extensions of the ideas expressed in the first three generalizations.

4. The variation in color and structure of these complex forms is the result of "hydrolysis" reactions, the extent of which depend on the strength of the acid involved.

5. Iron compounds of the weaker acids hydrolyze to such an extent that substances approaching colloidal dimensions are formed and exhibit the properties of colloidal particles.

It is not the purpose of this paper to consider the exact formula of each individual combination in detail. However, a division into groups is rather easily made and is of some value. The arrangement has been based upon the information contained in Table X, as applied to the results obtained in these experiments. The following grouping of the acids and their effects is suggested:

<center>TABLE XII</center>

1. Strong Acids
    (Hydrochloric—Sulfuric)
    Trichloracetic—Dichloracetic
        pale green and yellowish green colors
        iron present mostly as Fe^{+++}
        probably some in complex anions, such as
        $[Fe(C_2O_2Cl_3)_6]^{\equiv}$

2. Intermediate Strengths
    (a) Oxalic—Malonic
        green colors
        iron in very stable anions, such as $[Fe(C_2O_4)_3]^{\equiv}$
    (b) Maleic—Chloracetic
        red in concentrated solutions
        green in dilute solutions
        iron in both cations and anions, such as
        $[Fe_3(C_4H_2O_4)_3]^{+++}$, $[Fe(C_4H_2O_4)_3]^{\equiv}$
        anions more abundant
    (c) Formic—Tricarballylic
        red colors
        iron in both cations and anions, such as
        $[Fe_3(CHO_2)_6(OH)_2]^+$, $[Fe(CHO_2)_6]^{\equiv}$
        (cations more abundant)

2. Weak Acids
    Acetic—Propionic—Butyric
    Succinic—Glutaric—Adipic
    red colors
    iron in hydrolyzed cations, such as $[Fe_3(C_2H_3O_2)_6(OH)_2]^+$
    and possibly some as colloidal ferric hydroxide.

Most of the remaining acids tested—fumaric, mesaconic, benzoic, phenyl-acetic, and phthalic—probably belong in the third group, but the information obtained regarding them was comparatively meagre and they are omitted from the classification.

Summary

This work had for its purpose the collection of more information about the forms in which iron exists in organic acid solutions with particular attention to the possibilities of complex formation and of colloidal properties. The colors of these solutions, the colors on dilution and on concentration, and the relative color intensities were determined for a number of combinations. Experiments involving dialysis, light reflection, diffusion and electrolysis were also used as methods of comparison. Finally, a compilation was made of the formulas proposed by other investigators.

The conclusions drawn from this work were of a very general nature. They are best summarized in Table XI, which indicates the relationships between various complex forms, and in Table XII, which divides the individuals into groups upon the basis of acid strengths and the properties dependent thereon.

University of Colorado,
Boulder, Colorado.

THE EFFECT OF AQUEOUS SOLUTIONS
ON COLLOIDAL POWDERS*

BY J. L. SHERESHEFSKY

Agricultural chemists and geologists have been interested in the property of soils and geologic formations for taking up moisture, and have carried out a number of studies on the quantity of liquid imbibed and on the rate with which the liquid is absorbed.

The methods used in these studies consisted mainly in following the changes in pressure taking place in the cell containing the material, or in the vessel which supplies the liquid. Thus, W. Spring[1] employs a vessel which is provided with a membrane bottom and is connected at the top to a manometer. The material is packed into this vessel and then dipped into water. As the liquid is being taken up, the pressure change which takes place in the cell is followed on the manometer. Joffe and McLean[2] reversed the process by inserting into the material a porous cup filled with water and connected to a manometer. As the colloidal material absorbed the liquid, the pressure in the porous cup diminished. H. Freundlich and W. Sachs[3] improved the latter method by bringing the cell containing the liquid in contact with another vessel of definite thickness containing the colloidal material.

Both methods required accurate temperature control, since they involved changes in gas pressure, and were not suitable for an accurate determination of the total quantity of liquid absorbed. Furthermore, escaping gas bubbles from the pores of the material tend to clog the pores of the membrane in the apparatus of Freundlich and Sachs and thereby introduce inaccuracies in the rate determinations.

It was therefore desirable to devise an apparatus that would eliminate these difficulties and that would also make possible direct measurements of volumes absorbed at various intervals. It was further of interest to investigate the effect of aqueous salts solutions on the rate of sorption of a colloidal clay known to geologists as Jackson shale.

The Apparatus

The sorptometer as illustrated in Fig. 1 consists of a burette, A, whose smallest division reads .05 cc. To this burette there is connected, by means of the side arm B and the ground joint G, a cup F, containing a porous plate, D. The liquid or solution is introduced into the burette until it fills the apparatus to the top of the porous plate. If air bubbles remain below

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[1] Ann. Soc. Geol. Belg., **28** (1901); **29** (1902); Bull. Soc. Bel. Geol., **17** (1903).

[2] Soil Science, **20**, 169 (1925).

[3] Z. physik. Chem., **145A**, 177 (1929).

the plate, they may be removed by suction applied at the mouth of the cup, or by inverting the apparatus and allowing the bubbles to enter the burette. The stop-cock S is opened, and excess liquid is allowed to escape until there is no superfluous liquid on the surface of the membrane. This may be easily accomplished by having the level of the liquid in the burette slightly lower than the upper surface of the membrane. The material under investigation is closely packed into cell C, which is a glass cylinder provided with a bottom made of perforated filter paper. An ordinary glass plate placed above the
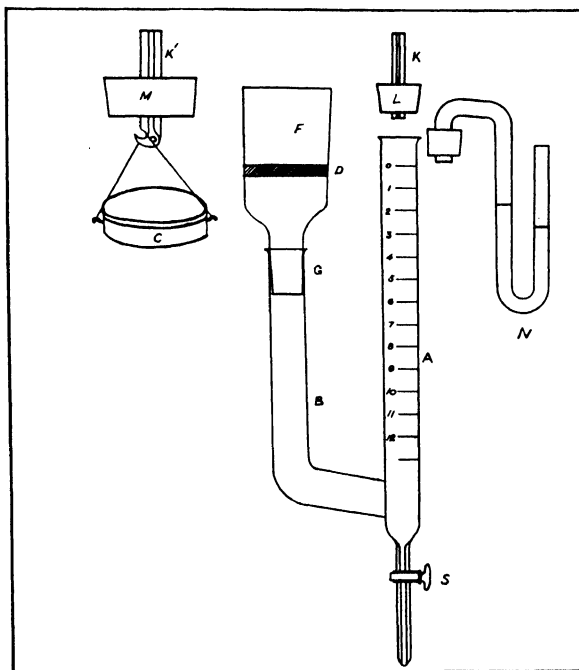
FIG. 1

Sorptometer A-Burette, B-Side Arm, F-Cup, D-Diaphram, G-Ground Joint, S-Stop-cock, N-Manometer, L and M-Stoppers, C-Cell, K and K'-Capillaries.

colloidal substance served as a top. Stopper L with the capillary tube K is placed in position to prevent evaporation, and the level of the liquid in the burette is noted. The cell C is now picked up by means of the hook on stopper M and is placed in cup F without having the cell touch the membrane D. Now, with stop-watch in one hand, the stopper M is put in full position, and timing is begun the moment cell C touches the porous plate D. The capillary in stopper M is to insure atmospheric pressure in the cell, and also to prevent loss of liquid by evaporation. As the liquid is being absorbed by the substance in the cell, the level in the burette drops, and the position of the meniscus is read at desirable intervals.

The maximum drop in the level of the liquid is conditioned by the largest pore in the membrane, and the surface tension of the liquid, since the pressure difference that may be maintained is given by

$$p = 2\,\sigma/r$$

where p is the pressure difference, σ the surface tension, and r the radius of the largest pore in the membrane. If the liquid level in the burette drops below the minimum level, gas bubbles will appear underneath the membrane. If it is desirable to work with large samples of colloidal material, it is necessary to select a porous membrane with suitably smaller pores, or, when great accuracy in reading the volume of the liquid is not essential, the burette may be changed to one of larger diameter.

The volumetric sorptometer may be easily changed into one which is a combination of both the volume and pressure types. This may be accomplished by inserting manometer N in place of stopper L.

Experimental and Results

The Jackson shale was ground to 80 mesh, and allowed to come in equilibrium with the moisture in the atmosphere. This was determined by frequent weighing of a given sample until there was no further gain in weight.

The cell C, which was about 3 mm. high and 26 mm. in diameter, was closely packed with a weighed quantity of clay and then carefully lowered into the sorptometer. Readings on the burette were taken at frequent intervals the first thirty or sixty minutes, and then the experiment was allowed to stand overnight. To account for the possible loss of liquid due to evaporation, the apparatus was allowed to stand for twenty-four more hours, and loss of liquid due to evaporation noted. From the total number of hours the experiment was allowed to go and the evaporation correction noted, the total volume imbibed was determined.

The temperature was that of the room, and very seldom varied more than one degree centigrade, since the apparatus was kept under a closed hood protected from air currents. Furthermore, temperature corrections were made, whenever the temperature of the final volume reading differed from that of the first reading by more than one degree.

TABLE I

The Rate of Sorption of Distilled Water

Wt. of Clay 2.3394 grams	Temp. 26° C	Wt. of Clay 2.3394 grams	Temp. 26° C
Time in min.	Volume in cc.	Time in min.	Volume in cc.
.25	.40	10	.93
.50	.45	16	1.08
1.0	.50	20	1.17
2.5	.63	70	1.55
5.0	.76	90	1.59
7.0	.84	23 hours	1.90

In Table I are given the volumes of pure water imbibed at various intervals. In Tables II and III are given the results of experiments with aqueous solutions of sodium chloride and magnesium chloride respectively.

TABLE II

The Rate of Sorption of Aqueous Solutions of NaCl

Wt. of Clay in grams	2.3385	2.3390	2.3383	2.3380	2.3380	2.3385	2.3385
Temperature °C	25–26	26	25.5	22	22	21.5	22.5
Normality	.001	.01	.05	.1	.2	.3	.5
Time in min.	Volume of Solution imbibed, cc.						
0	0	0	0	0	0	0	0
.25	.52	.51	.57	.90	1.19	1.12	1.18
.50	.57	.57	.68	1.14	1.30	1.20*	1.22
.75	—	—	—	—	1.33	1.26	1.26
1.00	.64	.65	.90	1.29	1.36	1.28	—
2.00	.72	.74	1.09	1.37	1.39	1.32	1.29
3.00	.77	.82	1.22	1.40	—	—	—
5.00	.87	.92	1.35	1.43	1.41	1.35	—
7.00	.95	1.00	1.40	1.44	—	—	—
10.00	1.04	1.11	1.45	—	—	1.36	1.33
15.00	1.18	1.25	1.49	1.45	1.43	—	—
20.00	—	1.35	1.51	—	—	—	—
25.00	1.38	1.43	1.52	—	—	—	—
30.00	1.45	1.48	1.52	—	—	—	—
40.00	1.53	1.53	—	—	—	—	—
50.00	—	1.56	—	—	—	—	—
60.00	1.60	—	—	—	—	—	—
Final Volume	2.13	1.92	1.84	1.56	1.61	1.52	1.45
Final Time in Hours	42	43	41	23	41	23	68

*25 sec.

TABLE III

The Rate of Sorption of Aqueous Solutions of MgCl₂

Wt. of Clay in grams	2.3385	2.3385	2.3385	2.3385	2.3385	2.3385
Temperature °C	24	26	28	28–29	26	28
Normality	.001	.01	.05	.1	.3	.5
Time in min.	Vol. of Solution imbibed in cc.					
0	0	0	0	0	0	0
.25	.50	.59	.90	.95**	1.16**	1.23
.50	.54	.66	—	1.27	1.28	1.28
.75	.57	.69	1.10	1.32	1.31	—
1.00	.59	.72	1.16	1.35	—	1.31
2.00	.67	.80	1.30	1.41	1.34	1.34
3.00	.71	.86	1.37	1.43	—	—
5.00	.81	.94	1.42	1.45	1.36	—
7.00	.87	1.02	1.45	—	—	—
10.00	.96	1.18*	1.49	1.47	—	—
15.00	1.09	1.24	—	1.48	1.37	1.37
20.00	1.19	1.34	—	—	—	—
25.00	1.26	1.40	1.52	—	—	—
30.00	1.34	1.44	1.52	—	—	—
40.00	1.40	1.47	—	—	—	—
50.00	1.45	—	—	—	—	—
60.00	—	—	—	—	—	—
Final Volume	1.86	1.84	1.63	1.57	1.51	1.39
Final Time in Hours	67	45	42	67	42	25

*12 min.   **10 sec.

The results obtained are rather interesting. As it will be observed, the rate of sorption increases with concentration, reaches a maximum, and then decreases. This is true for both the sodium chloride and the magnesium chloride solutions. The accelerated rate of sorptions as related to concentrations is illustrated in Fig. 2, where curve H is that of pure water, and B, C and D are those of .001 N, .05 N, and .2 N sodium chloride solutions respectively.

It will be observed also, by comparing Tables II and III, that the rate of sorption at equal concentrations is greater for magnesium chloride than for sodium chloride. Curves A and B represent the rates of sorption of .01 N sodium chloride and magnesium chloride respectively, and C and D are the curves for .05 N solutions of sodium chloride and magnesium chloride respectively.
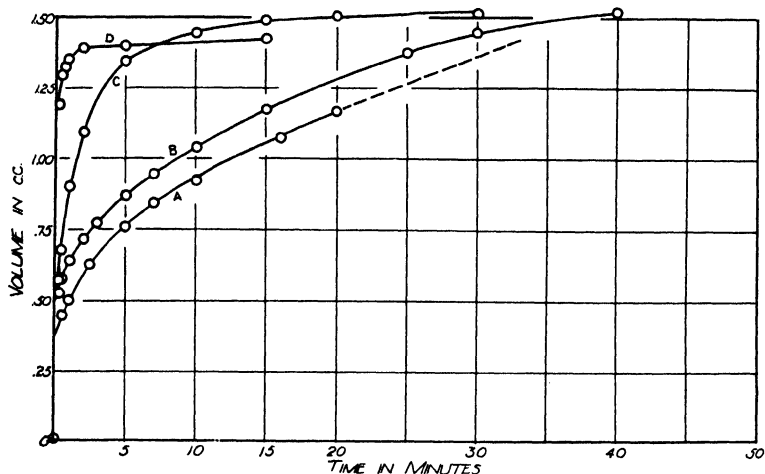
Fig. 2

The Imbibition of NaCl Solutions by Jackson Shale; A, distilled water; B, .001 N
NaCl; C, .05 N NaCl; D, .2 N NaCl.

Furthermore, it is to be noted that the final volume imbibed is also
dependent upon the concentration. In the case of sodium chloride, the
volume rapidly increases, reaches a maximum, and then decreases quite
gradually. In the case of magnesium chloride solutions no maximum is
observed, as shown in Fig. 4.
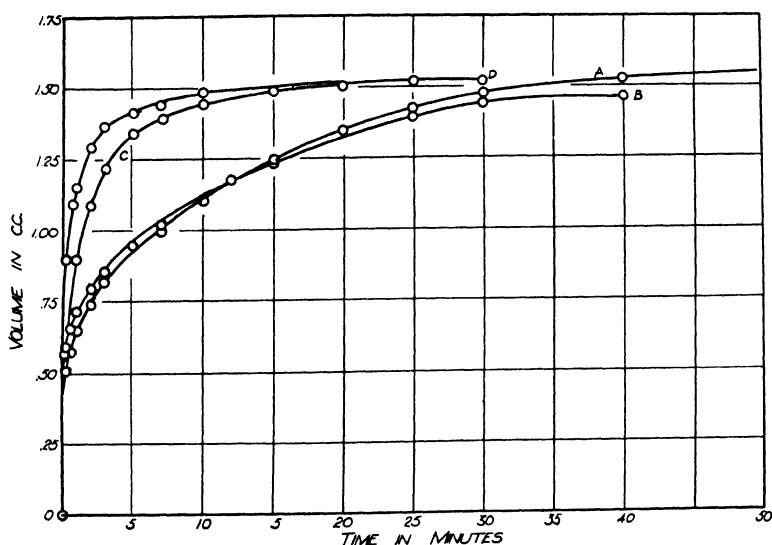
Fig. 3

The Imbibition of NaCl and MgCl₂ by Jackson Shale at equimolar Concentrations;
A, .01 N NaCl; B, .01 N MgCl₂; C, .05 N NaCl; D, .05 N MgCl₂.

The behavior of the clay towards electrolyte solutions as described above is so similar to colloidal behavior that Freundlich and Sachs[1] suggested it to be completely analogous to the behavior of suspensions. Assuming that the clay consists of aggregates of fine colloidal particles, the electrolyte solution tends to discharge them and cause their coalescence. As a result larger pores are formed in the clay, which is responsible for the increased rate of sorption. The maximum rate would therefore correspond to maximum coagulation. The maximum for magnesium chloride was about o.2 N, and for sodium
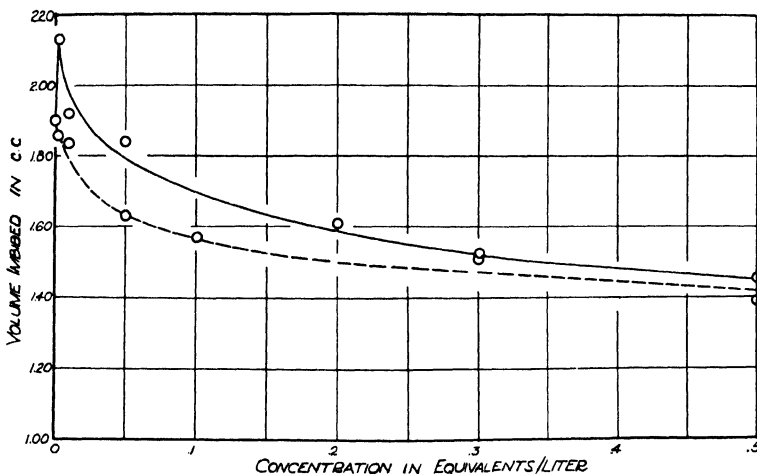
FIG. 4

Imbibition of NaCl and MgCl₂ Solutions at Various Concentrations; full line, NaCl Solutions; broken line, MgCl₂ Solutions.

chloride about o.3 N. Higher concentrations, because of the greater viscosity, tend to retard the rate of sorption.

The total volume imbibed seems to be connected with the phenomenon of swelling. The imbibition of .oo1 N and .o5 N sodium chloride solutions was accompanied by noticeable swelling of the total mass of clay. With the more concentrated solutions of sodium chloride and with all concentrations of magnesium chloride no swelling was observed. On the contrary, the sorption in the latter cases was accompanied by a contraction in volume.

Summary

Methods of measuring rate of sorption of colloidal powders are reviewed.

The construction of a volumetric sorptometer is described.

The effect of solutions of sodium chloride and magnesium chloride on the rate of sorption of Jackson shale is studied.

The mechanism of sorption of colloidal powders is discussed.

Washington, D. C.
November, 1931.

[1] Loc. cit.

A STUDY OF THE MECHANISM OF THE CATALYTIC DECOMPOSITION OF ESTERS BY NICKEL. III.

BY J. N. PEARCE AND HENRY J. WING[1]

Sabatier and Mailhe[2] have stated that the vapors of formic esters when passed over nickel may decompose in two ways,

$$(1) \quad 2\ HCOOC_nH_{2n+1} = HCOH + CO_2 + (C_nH_{2n+1})_2O, \text{ and}$$

$$(2) \quad HCOOC_nH_{2n+1} = CO + C_nH_{2n+1}OH.$$
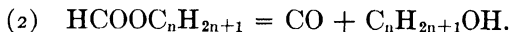
While both reactions may take place simultaneously, the latter is presumed to be the principal reaction, the decomposition proceeding rapidly above $220°$. The extent to which reaction (1) occurs at the threshold temperature of the decomposition will be indicated by the amount of carbon dioxide present in the resulting gaseous mixtures.

Sabatier and Senderens[3] find that methyl alcohol is decomposed by nickel at $180°$ to formaldehyde and hydrogen, but that more than two-thirds of the aldehyde formed is further decomposed to carbon monoxide and hydrogen. The effluent gaseous mixture contains hydrogen, carbon monoxide and a trace of methane due to the hydrogenation of a small amount of carbon monoxide. At $250°$ the reaction is even more rapid and eight-ninths of the aldehyde is decomposed. The gaseous products at this temperature are hydrogen, carbon monoxide, methane, and carbon dioxide, the latter to the extent of 1.7 by percent volume. At $350°$ methyl alcohol is completely decomposed, the aldehyde no longer survives and even the carbon monoxide has completely disappeared leaving behind a deposit of carbon on the nickel. They have also found that ethyl alcohol vapor in contact with nickel begins to decompose at $150°$ and that the velocity then gradually increases with the temperature. At $178°$ the condensate contains a certain proportion of aldehyde, a part of that formed having decomposed to hydrogen, methane, and carbon monoxide; but no carbon dioxide is present. Theoretically, the percentage by volume of the carbon monoxide and the methane should be the same. The excess volume of methane over that of carbon monoxide is due to the hydrogenation of the latter. Above $330°$ the amount of acetaldehyde condensed is a minimum and the resulting gaseous products are carbon dioxide, methane, and hydrogen, with only a trace of carbon monoxide. Propyl and butyl alcohols behave similarly in the presence of nickel.

The steps leading to the complete decomposition of an alcohol should be, and apparently they are:

$$(3) \quad C_nH_{2n+1}CH_2OH = C_nH_{2n+1}\ CHO + H_2, \text{ followed by}$$

$$(4) \quad C_nH_{2n+1}\ CHO = CO + C_nH_{2n+1}.$$

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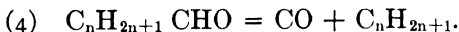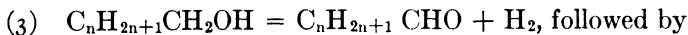
[1] Present address, The United States Bureau of Standards, Washington, D. C.

[2] Sabatier and Mailhe: Compt. rend., 154, 49 (1912); Sabatier and Reid: "Catalysis in Organic Chemistry," 14, 125 (1923).

[3] Sabatier and Senderens: Ann. Chim. Phys., (8) 4, 468 (1905).

If no secondary reactions occur, the ultimate decomposition products of an alcohol at its threshold decomposition temperature should be hydrogen, carbon monoxide, and a hydrocarbon containing one less carbon atom than the original alcohol molecule. It is interesting to note in passing that the temperature, 180°, at which methyl alcohol is only slightly decomposed is also the temperature at which the hydrogenation of the aliphatic aldehydes proceeds rapidly in the presence of nickel.[4]

Bancroft[5] states that in the decomposition of esters by nickel the following reactions are involved:

$$CH_3COOCH_2CH_3 = CH_3CH_2CH_3 + CO_2,$$

$$CH_3COOCH_3 = CH_3CH_3 + CO_2,$$

$$HCOOCH_3 = CH_4 \ (?) + CO_2.$$
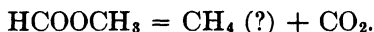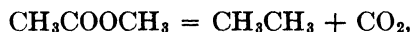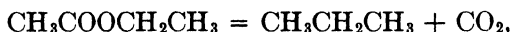
According to such a scheme one product of the decomposition must always be carbon dioxide. Another product will be a hydrocarbon formed by the union of the two alkyl residues left after the splitting out of the carbon dioxide. If no other reactions occur, the products should consist solely of carbon dioxide and a hydrocarbon. Moreover, if the decomposition of the ester in the presence of nickel is monomolecular, as it has been found to be,[6] the hydrocarbon must always contain more carbon atoms than does the highest alkyl group present in the original molecule. From the results of this and of previous investigations we may safely state that the mechanism pictured by Bancroft surely does not apply for the threshold decomposition temperatures.

In drawing conclusions as to the mechanism of decomposition from the nature and quantity of the products formed at the different temperatures we must always keep in mind the possibility of side reactions. Three such reactions are conspicuously present in the decomposition reactions under consideration.

Mond, Lange and Quincke[7] have found that the reaction,

$$(5) \quad 2 \ CO = CO_2 + C,$$
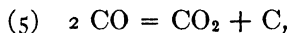
is accelerated by nickel between 350° and 450°. Sabatier and Senderens[8] have reported that the decomposition begins at temperatures as low as 180°. In a later paper[9] they also state that this reaction takes place over reduced nickel at 230°, and that further elevation of temperature accelerates the decomposition, which is complete at 350°, if the flow of the gas over the catalyst is sufficiently slow. Bahr and Bahr[10] assume the formation of a nickel carbide, Ni_3C,

$$(6) \quad 2 \ CO + 3 \ Ni = Ni_3C + CO_2,$$

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[4] Rideal and Taylor: "Catalysis in Theory and Practice," 209 (1919).

[5] Bancroft, see Sabatier and Reid: "Catalysis in Organic Chemistry," p. 65.

[6] Shinkichi, Horiba and Taikei: Bull. Chem. Soc. Japan, 3, 1825 (1928).

[7] Mond, Lange and Quincke: Chem. News, 62, 95 (1890).

[8] Sabatier and Senderens: Compt. rend., 134, 514 (1902).

[9] Sabatier and Senderens: Bull., (3), 29, 294 (1903).

[10] Bahr and Bahr: Ber., 61, 2177 (1928).

which decomposes at temperatures above 300°, giving free carbon and metallic nickel. They claim that the catalytic property of the nickel is due to the formation of a still more complex, unstable carbide, Ni_3C_x. Reactions (5) and (6) proceed more rapidly at higher temperatures; between 180° and 300°, however, they found the decomposition of carbon monoxide to be very slow.

The reaction between carbon monoxide and hydrogen in the presence of nickel[11] begins at temperatures as low as 180°-200°. It proceeds easily and rapidly at 230°-250°, yielding exclusively methane and water, if the volume of hydrogen added is equal to or exceeds that required for the stoichiometric proportions, thus

$$(7) \quad CO + 3\ H_2 = CH_4 + H_2O.$$
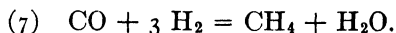
The reaction is found to be less complete when the carbon monoxide is present in excess, a part of the hydrogen passing through the catalyst unchanged.

The direct hydrogenation of carbon dioxide takes place under analogous conditions,[10] but it begins at a slightly higher temperature, 230°; it proceeds rapidly at 300°, also yielding methane and water,

$$(8) \quad CO_2 + 4H_2 = CH_4 + 2H_2O.$$
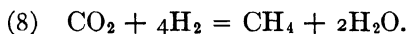
Pearce and Ott[12] have investigated the catalytic decomposition of certain esters by nickel. In this they were guided by the belief that any ester molecule is stable in the presence of reduced nickel up to a characteristic minimum threshold decomposition temperature. Since doubtless no two linkages of an ester molecule can be equally weak, the initial split in the molecule must occur between those two atoms or groups which are most feebly held together when the molecule is heated to the minimum temperature at which decomposition begins. From a study of the decomposition products obtained at various temperatures they have concluded that in the initial, and probably the only, decomposition of the ester molecule itself there is a primary cleavage of the molecule yielding momentarily a free alkyl and a free formic ester radical, e.g.,

$$(9) \quad RCH_2CO_2C_nH_{2n+1} = RCH_2{\rightarrow} + {\leftarrow}CO_2C_nH_{2n+1}.$$

These free radicals then unite with hydrogen to form the saturated hydrocarbon and an ester of formic acid. The results of their experiments carried out at high temperatures appeared to indicate that the mechanism of the further decomposition of the formic esters can be represented by a series of successive reactions as shown by equations (2), (3) and (4). The addition of hydrogen to the vapor before passing over the nickel does not in any way change the nature of the products. The hydrogen used in hydrogenating the radicals of (9) comes from the decomposition of the $RCH_2{\rightarrow}$. Their results also show that in the initial cleavage of the ester molecule no carbon dioxide should be evolved. The carbon dioxide present in the effluent gases is due to the subsequent decomposition of the carbon monoxide.

[11] Sabatier and Senderens: Ann. Chim. Phys., (8), **4**, 421, 425 (1905).
[12] Pearce and Ott: J. Phys. Chem., **28**, 1201 (1924); **31**, 102 (1927).

It is evident that the final test of the theory lies in a study of the catalytic decomposition of the formic esters and of the acetates at low temperatures. To this end we have made a careful study of the catalytic decomposition of methyl and ethyl formate, methyl and ethyl acetate, and ethyl alcohol at definitely controlled temperatures and with different samples of the same catalyst.

Materials and Apparatus

The esters used in this work were obtained directly from the Eastman Kodak Company. All except the methyl formate were washed and dried according to the methods described in the previous paper;[12] the methyl formate was purified by fractionation only. All of the esters were fractionated through a double-walled, silvered and evacuated, fractionating column;[13] the 85 cm. tube being packed with small sections of 5 mm. glass tubing. The ratio of the reflux to the product was regulated in a manner similar to that described by Marshall.[14] Only the middle fractions of the esters distilling over at the following temperatures were used: methyl formate, 31.10° at 748.6 mm.; ethyl formate, 53.63°–53.67° at 754.4 mm.; methyl acetate, 56.13° – 56.17° at 742.3 mm., and ethyl acetate, 76.80° at 748.6 mm.

A large sample of so-called absolute alcohol was further purified by refluxing with metallic calcium according to the method suggested by Smith;[15] the final distillate was kept sealed until used.

A large stock supply of pure nickel nitrate was prepared by recrystallization of the C.P. salt from solutions made slightly acid with nitric acid. One hundred grams of the purified salt were dissolved in 600 cc. of water, 100 g. of 20-mesh pumice were added and the whole evaporated to dryness. The mixture was then heated to dull redness until the oxides of nitrogen ceased to be evolved. Finally, the impregnated pumice was heated in a nickel crucible by a strong blast flame. Enough of this material was prepared at the beginning of the investigation so that all experiments were made with catalysts from the same source. The catalytic nickel used in each experiment was prepared by the reduction, *in situ*, of the oxide impregnated in the pumice.

Hydrogen gas was generated by the electrolysis of a concentrated solution of sodium hydroxide. The gas was washed, passed through concentrated sulphuric acid and then over a heated tungsten spiral. It was finally dried by passing through concentrated sulphuric acid and then successively over anhydrous calcium chloride and solid, flake sodium hydroxide.

The glass parts of the apparatus used are shown in Fig. 1. The 20 mm. pyrex catalyst tube was sealed to a smaller 8 mm. tube of approximately one half its length. A perforated disk was sealed in at G. Through this disk a hole was drilled which just permitted the passage of the tube E which inclosed the calibrated triple-junction copper-constantan thermocouple. The entire space between the disk G and the seal to the smaller tube was filled with the

[13] Loveless: Ind. Eng. Chem., **18**, 826 (1926).

[14] Marshall: Ind. Eng. Chem., **20**, 1379 (1928).

[15] Smith: Ind. Eng. Chem., Anal. Ed., **1**, 72 (1929).

impregnated pumice. In this way the thermocouple was completely surrounded by the catalyst material, which enabled us to read temperatures within the catalyst mass rather than upon its surface.

The catalyst tube, charged with the unreduced nickel oxide, was then placed in a 75 cm. tube furnace, connected in series with a variable resistance to the 110-volt lighting circuit. The temperature of the furnace was maintained constant at any desired temperature to within ± 1.0° by means of the closed system mercury regulator H. This regulator was similar to the one described by Wing,[16] except that it was entirely filled with mercury.
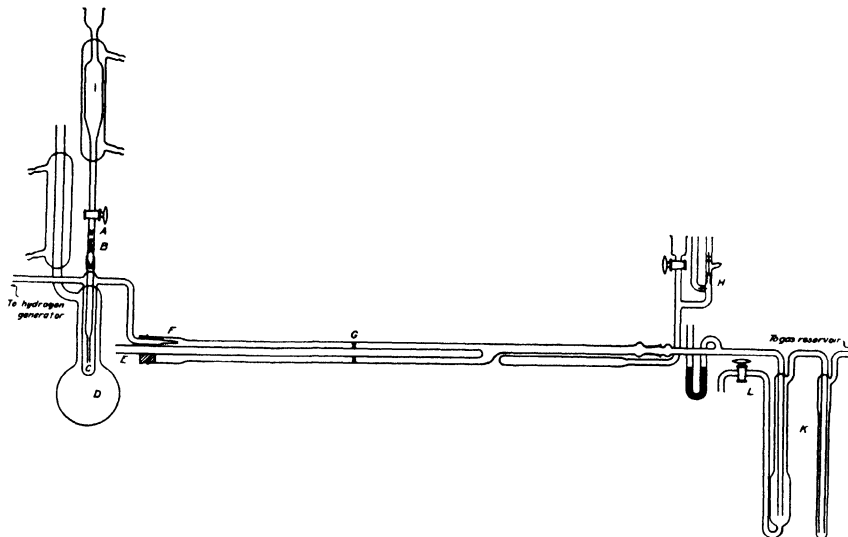
FIG. 1

The liquid ester was placed in a specially designed, water-jacketed, 25 cc. dropping pipette. The capillary tip A enables one to judge the speed of flow of the ester, while the small tube B serves to maintain a more regular flow into the vaporizing chamber C. The chamber C was kept at a temperature 20° to 30° above the boiling point of the ester by means of a suitable boiling liquid in the flask D. Condensation of the vapor in the enlarged end F of the catalyst tube was prevented by means of a small heating coil connected in series with the heater of the vaporizing chamber.

Two glass condensing tubes K, immersed in an ice bath, were used to collect the unchanged ester and liquid decomposition products. In no case, however, did any liquid condense in the second tube. The first condensing tube was so constructed that portions of the liquid products could be removed through L and analyzed during the course of the experiment.

The gases were analyzed by means of the modified form of the Burrell gas apparatus used in the previous work.[12] In this research, however, the gases were collected over mercury, and the confining liquid in the gas burette was also mercury.

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[16] Wing: Ind. Eng. Chem., Anal. Ed., 2, 196 (1930).

Experimental Procedure

Fifty cc. of the prepared pumice were placed in the catalyst tube. This was then placed in the furnace, the temperature was adjusted to 330° and the nickel oxide was reduced by means of a stream of dry hydrogen. The nickel was reduced at this same temperature in every experiment. Although the reduction was complete at the end of three hours, as indicated by the absence of further formation of water; the hydrogen was allowed to pass for four hours to insure complete reduction. Once the oxide was reduced, the passage of the hydrogen was continued until the ester vapor was started through the catalyst.

The furnace temperature was reduced to that chosen for the experiment, the hydrogen was turned off and the ester vapor started. In each experiment the ester vapor was passed for one and one-half hours before the gaseous products were collected for analysis. This procedure prevented the entrance of air or other gases to the catalyst. The products were led through the condensation tubes, surrounded by ice and water, where the liquefiable portion was condensed; the gaseous products were collected over mercury and later analyzed.

The liquids which were condensed in the ice trap were also analyzed. In the experiments with the methyl and ethyl acetates the liquid products were found to be the unchanged esters, as previously reported; the boiling points were practically identical with those of the original esters. By the same test the properties of the liquid products from the other three substances were found to differ widely from those of the pure compounds. That reducing materials were present was shown by the action of the water soluble portion on an ammoniacal solution of silver nitrate. These reducing agents were identified as formaldehyde or acetaldehyde by the methods of Mulliken.[17]

Experimental Results

The results of the analyses of the gaseous products of the four esters and the alcohol are shown in Tables I to V. The experimental temperatures are given in the top horizontal row; the vertical columns contain the percentages of the constituents indicated at the left. Each value is the mean of at least two independent determinations differing usually by not more than two percent and for the most part falling well below this limit. Moreover, each determination is made with a new sample of the reduced nickel. Since the speed with which the ester vapor passes over the catalyst was found to have a marked influence on the proportions of the various constituents in the effluent gases, the speed of flow of vapor was made as nearly as possible the same in the different experiments. Since no more than a trace of ethane was ever found, it is not indicated in the Tables. The percentages of "Unsat'd" constituents are negligibly small in all cases, and besides it is doubtful if unsaturated compounds could pass unreduced in the presence of hydrogen and nickel.

[17] Mulliken: "The Identification of Pure Organic Compounds," 1, 22, 24.

TABLE I
Gaseous Products from Methyl Formate

Temp.	152°	200°	250°	300°
CO_2	>1.0	>1.0	>1.0	>1.0
CO	67.7	72.4	58.5	55.3
H_2	29.3	24.8	39.1	41.1
CH_4	1.8	1.7	1.2	2.4
Unsat'd	0.1	0.1	0.1	0.1

TABLE II
Gaseous Products from Ethyl Formate

Temp.	152°	200°	250°	300°
CO_2	1.0	1.6	1.2	1.0
CO	60.1	64.9	51.9	49.6
H_2	38.3	28.7	26.0	22.2
CH_4	0.7	4.6	20.6	27.1
Unsat'd	trace	0.2	0.2	0.1

TABLE III
Gaseous Products from Methyl Acetate

Temp.	152°	200°	250°	300°
CO_2	*	1.1	1.7	8.5
CO	*	24.6	32.2	35.4
H_2	*	48.5	52.9	28.0
CH_4	*	25.7	13.2	28.1
Unsat'd	*	trace	trace	trace

*No decomposition.

TABLE IV
Gaseous Products from Ethyl Acetate

Temp.	152ᶜ	200°	250°	300°
CO_2	*	*	1.5	1.6
CO	*	*	35.0	31.6
H_2	*	*	37.9	45.4
CH_4	*	*	25.6	20.8
Unsat'd	*	*	trace	0.6

*No decomposition.

TABLE V
Gaseous Products from Ethyl Alcohol

Temp.	152°	200°	250°	300°
Co_2	0.0	0.0	trace	0.5
CO	5.2	18.8	31.5	33.2
H_2	89.7	64.8	39.5	28.3
CH_4	5.1	16.4	28.8	37.8
Unsat'd	0.0	0.0	0.2	0.2

At 300° in the case of the methyl and ethyl formates and ethyl alcohol only a small amount of liquid product was obtained, which indicated almost complete decomposition. The condensate from the ethyl alcohol decompositions at the three lower temperatures gave strong tests for acetaldehyde.[18]

Water in comparatively large amounts was present in the condensed product from the 300° decomposition of methyl and ethyl formate and ethyl alcohol. At the lower temperatures the condensates reacted to none of the usual tests for water.

The catalysts used with the acetates were darker at the end of the run than those used with the other vapors. This was due to the fact that larger amounts of carbon were deposited on the catalysts than were deposited in the other cases. The carbon was especially noticeable in the case of the ethyl acetate at 300°.

The decomposition of the ethyl acetate at 300° was unusual also in that, while the reaction began more rapidly than that with the same ester at 250°, it soon slowed down and came to a complete stop in about four hours. In no other experiment was there a noticeable decrease in the catalytic activity although in some cases the time was extended to six hours.

The lowest temperatures used with the various vapors are practically the lowest temperatures at which decomposition will take place, for the decomposition at these temperatures is very slow. These temperatures represent approximately the temperature thresholds at which the various esters begin to decompose.

Discussion

If the theory assumed for the mechanism of the catalytic decomposition of esters by nickel is correct, the decomposition of methyl formate should proceed in three steps:

$$HCOOCH_3 = CO + CH_3OH,$$
$$CH_3OH = H_2 + HCHO,$$
$$HCHO = CO + H_2.$$
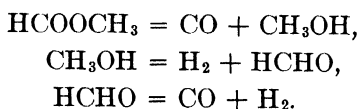
Likewise the decomposition steps for ethyl formate should be,

$$HCOOC_2H_5 = CO + C_2H_5OH,$$
$$C_2H_5OH = H_2 + CH_3CHO,$$
$$CH_3CHO = CO + CH_4.$$
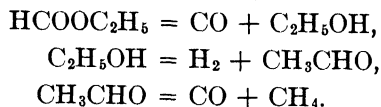
Thus if side reactions are absent, methyl formate should give only carbon monoxide and hydrogen. Ethyl formate should yield only carbon monoxide, hydrogen and methane. Carbon dioxide should not occur in the decomposition products of either ester.

The decomposition products of both formates show a small almost constant amount of carbon dioxide. The small amount present is almost within the experimental error of the method of analysis. However, its presence can be easily accounted for by the reaction shown in equation 5.

There is only a small amount of methane in the decomposition products of methyl formate. This is in accord with our theory. The methane in the

[18] Bancroft and George: J. Phys. Chem., **35**, 2194 (1931).

gaseous products from ethyl formate increases with rising temperature; however, at the same time the carbon monoxide and hydrogen show a pronounced decrease.

All the other decomposition schemes which have been formulated show carbon dioxide as one of the principal products of the decomposition. Under the conditions of our experiments, we have found carbon dioxide to be present in only small proportions in the decomposition products from the esters used. This would show that the mechanisms postulated by other writers can not represent the facts under the conditions of the present research. This one fact, the failure to form carbon dioxide, indicates that these reactions do not show the true relations. Equation (9).

(9) $CH_3COOC_2H_5 = CH_3 \rightarrow + \leftarrow COOC_2H_5$ explains this initial decomposition without requiring the formation of any carbon dioxide.

Further, it is to be noted that, under the conditions employed in this research, an increase in the temperature of decomposition of ethyl acetate decreases the percentage of methane and increases that of hydrogen in the product. This would seem to furnish further proof for the decomposition scheme as represented in (9). The explanation of the decrease in the methane content of the gas formed at 300° as compared with that formed at 250° may be found in the large amount of free carbon which was formed on the catalyst. This carbon can be accounted for by the reaction represented by the following equation:

$$(10) \quad 2\ CH_3 \rightarrow\ =\ 2\ C + 3\ H_2.$$
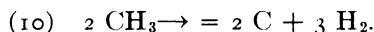
This reaction also enables us to explain the increase in hydrogen content of the product. The amount of unsaturated compounds increased from a trace to 0.6 per cent between 250° and 300°. This would indicate that some of the methyl radicals were only partially decomposed and the residues then united to form an unsaturated compound:

$$(11) \quad 2\ CH_3 \rightarrow\ =\ CH_2 : CH_2 + H_2.$$
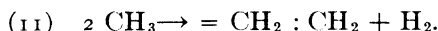
A complete diagrammatic plan of the decomposition of ethyl acetate, where the initial break in the molecule is that represented by (9), will include the following successive steps:

(a) $\quad CH_3COOC_2H_5 = CH_3 \rightarrow + \leftarrow COOC_2H_5$

(b) $\quad CH_3 \rightarrow + \leftarrow H = CH_4$

(c) $\quad H \rightarrow + \leftarrow COOC_2H_5 = HCOOC_2H_5$

(d) $\quad HCOOC_2H_5 = CO + C_2H_5OH$

(e) $\quad C_2H_5OH = H_2 + CH_3CHO$

(f) $\quad CH_3CHO = CO + CH_4$

Here it is seen that the two hydrogen atoms which are formed in the decomposition of the ethyl alcohol, (e), are equivalent to that required for the hydrogenation of the methyl and formate radicals, (b) and (c). Hence the hydrogen content of the effluent gas must be equivalent to that formed in the decomposition of the methyl radical as represented in equation (9) and (10).

Pearce and Ott[6] have already set forth a number of reasons for believing that the ester decomposition takes place according to equation (9). The

excessive deposition of carbon is found to take place only in the case of the acetates. This is additional proof, since this plan of decomposition, involving the primary release of a methyl radical, can take place only in the case of acetates. The fact that the catalyst was easily inactivated during the decomposition of the acetates may be explained on the assumption that the carbon deposited behaved as a catalyst poison.

The fact that water was formed in the decomposition of methyl and ethyl formate and of ethyl alcohol at 300°, while none was formed in the decomposition of methyl and ethyl acetates at the same temperatures may be explained in the following manner. If we assume with Langmuir[19] that the catalyst can activate only part of the hydrogen, then this hydrogen will attack that group which is itself most active. In the case of the acetates the $CH_3 \rightarrow$ radical formed in the initial split, (a), of the molecule is present. The carbon monoxide is a product of a later reaction, (d) or (f). In the case of the formates the initial decomposition does not give this $CH_3 \rightarrow$ radical, but instead yields carbon monoxide and an alcohol. The alcohols give first hydrogen and an aldehyde, which then decomposes to carbon monoxide and a hydrocarbon. The failure to form water in the decomposition of acetates can be explained on the assumption that as fast as the active hydrogen is formed it is used up in hydrogenating the $CH_3 \rightarrow$ radical. For this reason there is but little, if any, reduction of the carbon monoxide. Under these conditions no water should be formed, and we found none.

Engelder,[20] Sabatier and Senderens,[21] and Armstrong and Hildreth[22] have reported on the decomposition of ethyl alcohol. The results obtained in the present research are more in accord with those of the latter two investigators. Engelder reports 2.0% ethylene and 3.4% ethane in the products formed at 380°. The catalyst which we used did not give these products to any appreciable extent up to 300°.

Summary

1. The catalytic decomposition of methyl and ethyl formate, methyl and ethyl acetate, and ethyl alcohol by nickel has been studied at 152°, 200°, 250° and 300° and the products have been determined.

2. The approximate temperatures at which decomposition of the various substances begins have also been determined.

3. The scheme representing the various steps in the catalytic decomposition of esters by nickel appears to be definitely established. In its support we have shown the almost complete absence of carbon dioxide, at the low temperatures used, in the decomposition products from the formates and the acetates studied. The rapid inactivation of the catalyst and the formation of water, in the case of the acetates, are also in accord with it.

Physical Chemistry Laboratory,
The State University of Iowa.

[19] Langmuir: J. Am. Chem. Soc., **38**, 2287 (1916).
[20] Engelder: J. Phys. Chem., **21**, 681 (1917).
[21] Sabatier and Senderens: Ann. Chim. Phys., (8) **4**, 469 (1905).
[22] Armstrong and Hildreth: Proc. Roy, Soc., **97A**, 259 (1920).

THE MECHANISM OF THE MUTUAL COAGULATION
PROCESS. II.

BY HARRY B. WEISER AND THOMAS S. CHAPMAN

In a recent communication[1] dealing with the mutual coagulation process it was demonstrated that, when a given series of positive sols is arranged in order of the optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols may vary widely with different negative sols. It was shown further, that the zone of complete mutual coagulation of two sols of opposite sign may be quite narrow or very broad. The reason for the observed behavior is that the precipitating power of positive sols for negative sols is not determined exclusively by the charge on the colloidal particles. Other factors which influence the process are: (1) the interaction between stabilizing ions, (2) the presence in the sols of precipitating ions which were not removed in the process of preparation and purification, and (3) mutual adsorption of colloidal particles, that is independent of their charge. With reference to the first of these factors it was shown that complete mutual coagulation is not due in general to interaction with the consequent removal of the stabilizing electrolytes of the oppositely charged sols; but that this may be important in certain cases. The effect of unadsorbed electrolytes in the sols as a factor in the process will be considered in this paper. The third factor, mutual adsorption of particles that is determined by their specific nature rather than by their surface charge, must await consideration until some way is found for the quantitative evaluation of the mutual adsorption process.

In the preparation of hydrophobic sols which owe their charge to the preferential adsorption of ions, the peptization is accomplished by the presence of an electrolyte containing a relatively strongly adsorbed anion or cation. In general, the intermicellar solution will contain more or less of the peptizing electrolyte, the amount depending on the method of preparation and the extent of purification. The effect of such electrolyte impurities on the mutual coagulation process has been pretty generally overlooked although it may be a very important factor especially if one of the ions is multivalent. For example, if the excess alkali ferrocyanide used in the preparation of a negatively charged copper ferrocyanide sol is not removed completely and this sol is used to coagulate positive sols, the ferrocyanide ion in the intermicellar solution will exert a precipitating action on the positive sols that is independent of but supplements the mutual coagulation of the oppositely charged particles. In the earlier experiments the attempt was made to minimize this effect as far as possible by working with well purified sols.

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[1] J. Phys. Chem., **35**, 543 (1931).

In the following experiments, sols of varying purity were employed and the effect on the width of the mutual coagulation zone and the composition of the coagulum was determined.

Experimental

Preparation of Sols. Positive hydrous ferric oxide sol and negative sols of arsenic trisulfide, hydrous stannic oxide and copper ferrocyanide were prepared by the same procedure outlined in the paper to which reference has been made.[1] Hydrous alumina was formed by adding ammonia to a solution of aluminum chloride short of precipitation and dialyzing in the hot.[2] The purity of the sols was regulated by the time of dialysis. In the case of hydrous alumina and ferric oxide, eight or ten liters of sols were prepared and divided into a number of equal portions which were dialyzed simultaneously and continuously in the hot. From time to time samples were removed for analysis and the dialysis was stopped when the desired Cl/oxide ratio was attained.

Method of Procedure. The procedure followed in locating the zone of complete mutual coagulation was essentially the same as that described in the first paper. The sols were mixed always in such amounts that the total volume was 10 cc. The limits of the zone of mutual coagulation were first determined within 1 cc, after which a series of tests were made which located the limits of the zone to within 0.1 cc of the respective colloids. The mixing of the two portions of oppositely charged sols was made as rapidly as possible and the mixture was allowed to stand 30 minutes, after which it was centrifuged for 1 minute and the supernatant solution examined for complete coagulation. This was readily detected visually with colored sols but with colorless ones a portion of the sol was pipetted off, treated with an electrolyte having a multivalent precipitating ion and examined after a few minutes for the presence or absence of a floc. A typical example of the data obtained in a given case is shown in Table I.

TABLE I

Mutual Coagulation of Fe_2O_3 Sol and $Cu_2Fe(CN)_6$ Sol

Fe_2O_3 2.77 g/l cc	$Cu_2Fe(CN)_6$ 4.18 g/l cc	Observations	Range of complete mutual coagulation % Fe_2O_3 by weight
3.2	6.8	Excess $Cu_2Fe(CN)_6$ sol	
3.3	6.7	Complete mutual coagulation	
5.0	5.0	Complete mutual coagulation	24.6 to 39.9
5.1	4.9	Excess Fe_2O_3 sol	

Ferric Oxide Sol and Negative Sols.

Some preliminary experiments were carried out which indicate the effect of electrolyte impurities in the oppositely charged sols on the width of the mutual coagulation zone. Two samples of ferric oxide, stannic oxide, and

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[1] J. Phys. Chem., **35**, 543 (1931).

[2] Cf. Weiser: J. Phys. Chem., **35**, 1370 (1931).

copper ferrocyanide sols were prepared. One set of samples was relatively impure and is designated "impure"; the other set of samples, having been subjected to prolonged dialysis, was relatively pure and is referred to as "pure." The zone of mutual coagulation for all the possible combinations was determined and the results summarized in Table II and Fig. 1. Since the terms "pure" and "impure" as applied to the sols are relative, the results
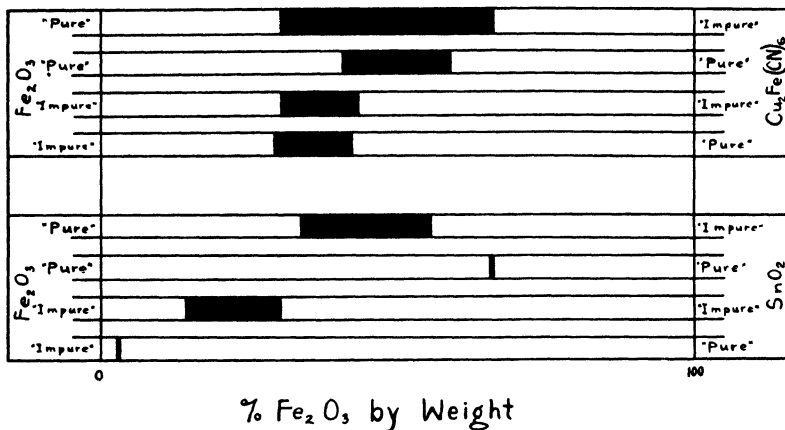
$$\% \ Fe_2O_3 \ by \ Weight$$

FIG. 1

Influence of Purity of Sols on the Range of Mutual Coagulation.

TABLE II

Mutual Coagulation of Positive and Negative Sols of Varying
Degrees of Purity

Positive sols	Negative sols	Range of complete mutual coagulation $\%$ Fe_2O_3 by weight
Fe_2O_3 "pure" 1.52 g/l	$Cu_2Fe(CN)_6$ "impure" 2.85 g/l	30.1 to 66.0
Fe_2O_3 "pure"	$Cu_2Fe(CN)_6$ "pure" 2.50 g/l	40.6 to 58.7
Fe_2O_3 "impure" 1.30 g/l	$Cu_2Fe(CN)_6$ "impure"	30.1 to 43.0
Fe_2O_3 "impure"	$Cu_2Fe(CN)_6$ "pure"	28.6 to 42.4
Fe_2O_3 "pure"	SnO_2 "impure" 3.23 g/l	33.4 to 55.2
Fe_2O_3 "pure"	SnO_2 "pure" 2.11 g/l	65.0 to 65.5
Fe_2O_3 "impure"	SnO_2 "impure"	14.2 to 30.0
Fe_2O_3 "impure"	SnO_2 "pure"	2.6 to 3.1

are qualitative; but they show the marked effect of purity of sol on the position and width of the zone of mutual coagulation. It will be noted that in general the zone is broadened by the presence in the intermicellar liquid of an electrolyte which contains an ion of high precipitating power.

Observations were next made with ferric oxide sols of varying degrees of purity as indicated by the Cl/Fe_2O_3 ratio, and the negative sols of copper ferrocyanide, stannic oxide, and arsenic trisulfide. In every case the negative

sols were prepared in such a way that they would be expected to be quite pure. Actually, however, in the nature of things the stannic oxide sol was the only one in which the intermicellar liquid was practically free from electrolyte. In the preparation of this sol only a small amount of NH_4OH was required for peptization of the hydrous oxide. The excess was removed by boiling and further purification was accomplished by dialysis. The As_2S_3 sol was washed with hydrogen to remove the excess H_2S. Unfortunately, the extent of purification of the sol is limited by the fact that As_2S_3 hydrolyzes. Hence if the H_2S content is reduced too low the intermicellar solution is contaminated with H_3AsO_3. The copper ferrocyanide sol was purified by prolonged dialysis in the cold but it still contained some of the peptizing electrolyte as evidenced by the fact that the sol gave the Prussian blue test promptly on adding a trace of ferric salt.

The results of a series of experiments carried out as indicated in Table I are summarized in Table III and reproduced graphically in Figs. 2, 3, and 4.

TABLE III

Coagulation of Positive Fe_2O_3 Sols of Varying Purity and Negative Sols

Positive Fe_2O_3 sol		Negative sol	Range of complete mutual coagulation % Fe_2O_3 by weight
Purity Cl/Fe_2O_3	g Fe_2O_3/l		
0.0615	2.77	$Cu_2Fe(CN)_6$ 4.18 g/l	24.6 to 39.9
0.0480	3.01	″	26.2 to 42.0
0.0402	2.83	″	24.2 to 39.5
0.0169	3.04	″	30.8 to 45.2
0.0071	3.03	″	36.4 to 55.1
0.0027	2.94	″	44.3 to 75.0
0.0615	2.77	As_2S_3 3.80 g/l	51.5 to 58.5
0.0480	3.01	″	52.3 to 56.1
0.0402	2.83	″	51.7 to 56.0
0.0169	3.04	″	50.5 to 57.4
0.0071	3.03	″	50.9 to 61.0
0.0027	2.94	″	54.9 to 93.5
0.0615	2.77	SnO_2 3.51 g/l	15.6 to 28.2
0.0480	3.01	″	14.3 to 29.6
0.0402	2.83	″	16.8 to 33.2
0.0169	3.04	″	34.8 to 51.4
0.0071	3.03	″	55.4 to 62.7
0.0027	2.94	″	76.0 to 77.0

These data demonstrate conclusively that as the electrolyte content of one sol is diminished the precipitating action of the other becomes more pronounced. Thus with the several negative sols the width of the zone of complete mutual coagulation remains almost constant with decreasing purity of the ferric oxide sol until the Cl/Fe_2O_3 ratio is approximately 0.02 at which
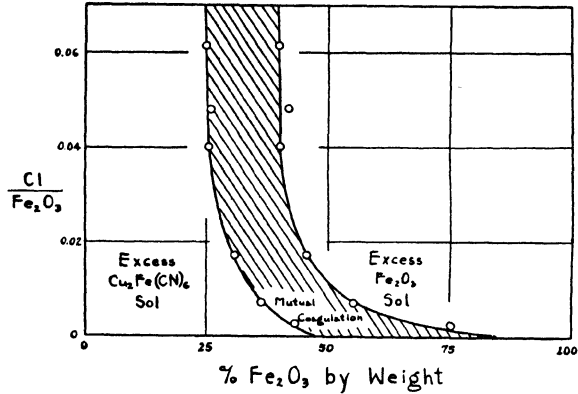
FIG. 2

Zone of Mutual Coagulation with Fe_2O_3 sols of Varying Purity and As_2S_3 Sol.
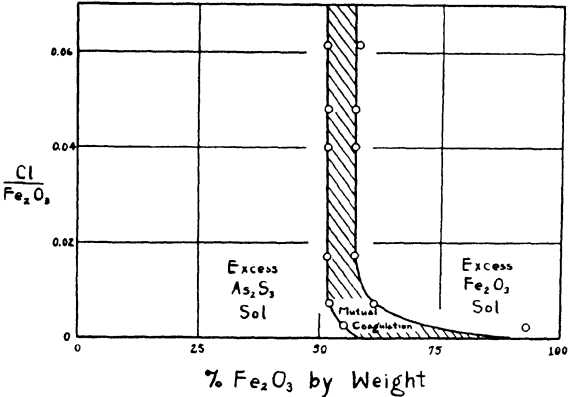
FIG. 3

Zone of Mutual Coagulation with Fe_2O_3 Sols of Varying Purity and As_2S_3 Sol.
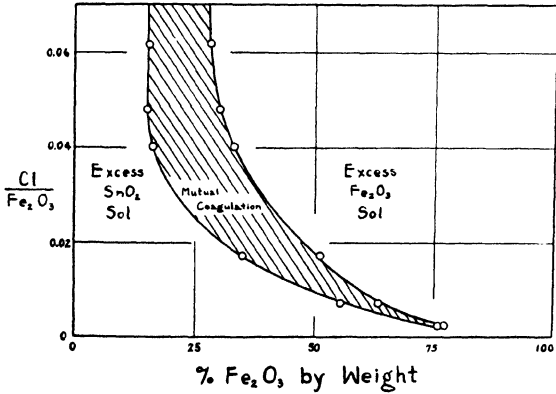
FIG. 4

Zone of Mutual Coagulation with Fe_2O_3 Sols of Varying Purity and SnO_2 Sol.

point the ultrafiltrate from the sol is free from chloride ion (HCl). The width of the zone then increases or decreases with further decrease in the Cl/Fe_2O_3 ratio depending on the purity of the negative sol. With the copper ferrocyanide sol containing a small excess of $K_4Fe(CN)_6$ and the As_2S_3 sol containing a small amount of H_3AsO_3 or H_2S, the zone widens out in the direction of greatly increasing the relative amount of Fe_2O_3 in the precipitate. This is probably due chiefly to the precipitating action of the electrolyte in the intermicellar solution. With the highly pure stannic oxide sol, on the other hand, the zone of complete mutual coagulation is narrowed down as the purity of the ferric oxide sol increases. This means that if one mixes two oppositely charged sols the ultrafiltrates from which contains little or no electrolyte, the zone of mutual coagulation will be narrow. In other words, if the mutual electrical neutralization of oppositely charged particles is the prime factor determining mutual coagulation, the zone will be relatively narrow.

Hydrous Alumina Sol and Negative Sols.

Observations similar to those with hydrous ferric oxide were made with alumina sols of varying purity. The data which are summarized in Table IV and shown graphically in Figs. 5, 6, and 7 confirm those obtained in the preceding section. It should be noted that the alumina sols were weaker, less pure, and had a higher precipitating power for the negative sols than

TABLE IV

Coagulation of Al_2O_3 Sols of Varying Purity and Negative Sols

Positive Al_2O_3 sol		Negative sols	Range of complete mutual coagulation
Purity	g Al_2O_3/l		% Al_2O_3 by weight
0.152	0.391	$Cu_2Fe(CN)_6$ 4.18 g/l	4.4 to 6.8
0.134	0.381	,,	4.7 to 7.5
0.0865	0.446	,,	7.2 to 12.0
0.0740	0.454	,,	8.2 to 14.5
0.0647	0.505	,,	8.8 to 28.8
0.0490	0.408	,,	10.6 to 25.7
0.152	0.391	As_2S_3 3.8 g/l	2.9 to 6.4
0.134	0.381	,,	4.9 to 6.9
0.0865	0.446	,,	7.4 to 14.0
0.0749	0.454	,,	8.3 to 17.5
0.0647	0.505	,,	9.8 to 19.8
0.0490	0.408	,,	11.6 to 14.9
0.152	0.391	SnO_2 3.51 g/l	6.3 to 9.7
0.134	0.381	,,	6.9 to 18.3
0.0865	0.446	,,	11.7 to 16.6
0.0740	0.454	,,	14.6 to 19.5
0.0647	0.505	,,	15.0 to 22.4
0.0490	0.408	,,	18.4 to 25.9
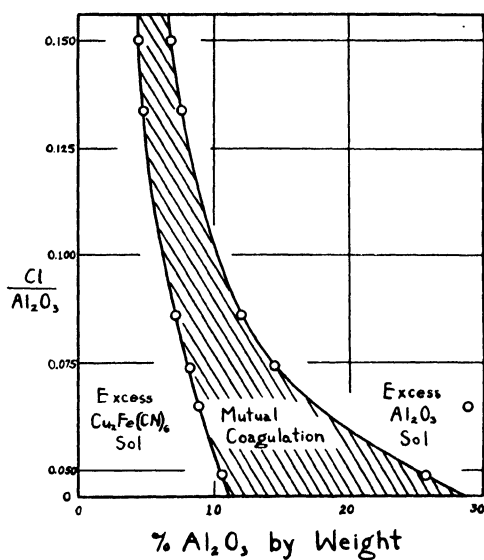
FIG. 5
Zone of Mutual Coagulation with Al_2O_3 Sols
of Varying Purity and $Cu_2Fe(CN)_6$ Sol.
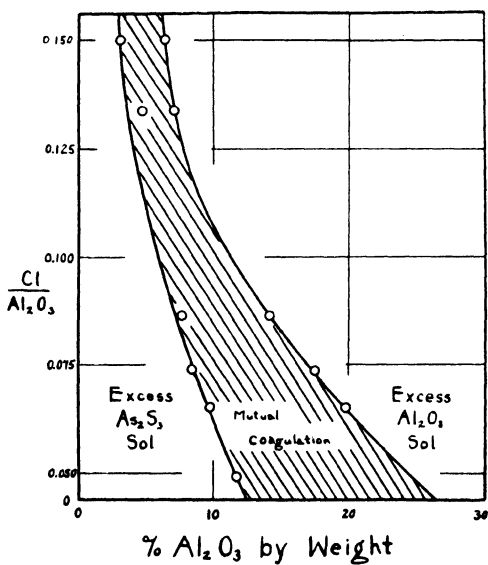
FIG. 6
Zone of Mutual Coagulation with Al_2O_3
Sols of Varying Purity and As_2S_3 Sol.
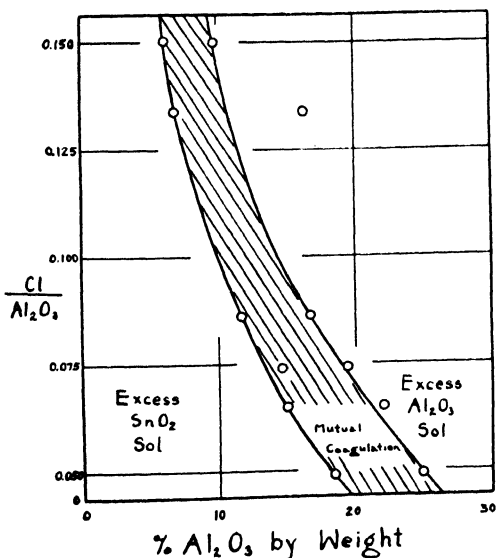
FIG. 7

Zone of Mutual Coagulation with Al₂O₃ Sols
of Varying Purity and SnO₂ Sol.

the ferric oxide sols. The purest alumina sol had a Cl/oxide ratio of 0.0490 while the purest ferric oxide sol had a Cl/oxide ratio of 0.0027. Moreover, the ultrafiltrates from all the alumina sols contained chloride. As in the case of the experiments with ferric oxide sols the zone of complete mutual coagulation widened in the direction of a higher percentage of alumina in the precipitate as the chloride content of the sol diminished. The zone did not narrow down sharply with stannic oxide and alumina as it did with the highly purified ferric oxide but with purest alumina the width of the zone was distinctly less with stannic oxide than with either arsenic trisulfide or copper ferrocyanide.

Summary and Conclusions

The following is a brief summary of the results of this investigation:

1. A study has been made of the effect on the mutual coagulation process of the presence of unadsorbed electrolytes in the sols.

2. The zone of complete mutual coagulation was determined for positive hydrous alumina and ferric oxide sols of varying purity and well purified negative sols of arsenic trisulfide, stannic oxide, and copper ferrocyanide.

3. The presence of free electrolytes in the oppositely charged sols has a marked effect on the width of the zone of mutual coagulation and the composition of the coagulum.

4. The zone of mutual coagulation is quite narrow if the intermicellar solution in both sols contains little or no free electrolyte or if the free electrolyte which is present contains ions of low precipitating power. In such

cases the electrical neutralization by mutual adsorption of oppositely charged colloidal particles is the prime factor in determining the mutual coagulation.

5. The zone of mutual coagulation is broad if one of the sols, say the positively charged sol, is quite pure and the negatively charged sol contains an electrolyte with an anion of high precipitating power. In this case the precipitating anion in the intermicellar solution exerts a coagulating action on the positive sol that is independent of but supplements the coagulation by mutual adsorption of oppositely charged particles.

6. When a given series of positive sols is arranged in the order of optimum concentration for mutual coagulation on mixing with negative sols, the order of the positive sols will be the same for different negative sols only in case the mutual coagulation process results primarily from mutual adsorption of oppositely charged colloidal particles.

7. Since the nature and amount of electrolyte impurities in oppositely charged sols has a marked effect on the width of the zone of mutual coagulation and the composition of the coagulum, it is not surprising that the order of precipitating power of a series of positive sols for different negative sols usually exhibits considerable variation.

The Rice Institute,
Houston, Texas.

THE TRANSFORMATION FROM BLUE TO ROSE
COBALTOUS HYDROXIDE

BY HARRY B. WEISER AND W. O. MILLIGAN

The addition of excess alkali to a solution of cobaltous salt gives a deep blue gelatinous precipitate which later turns to rose cobaltous hydroxide. Under certain conditions the highly hydrous precipitate appears green rather than blue. Winkelblech[1] concluded that the blue precipitate was a basic salt and that the green coloration often observed, was the result of partial oxidation. The first conclusion was disproven by Hantzsch[2] who showed that both the blue and rose precipitates were cobaltous hydroxide. The difference in color was explained by assuming that the blue is $CoO \cdot H_2O$ and the rose $Co(OH)_2$. Weiser[3] questioned the accuracy of this assumption and suggested that the variation in color may be due to a difference in particle size. The cause of the various colors of the hydroxide has been the basis of recent independent studies by Stillwell,[4] and by Hüttig and Kassler.[5]

As a result of microscopic and x-ray examinations of the precipitates formed by the interaction of alkali and cobaltous salts under varying conditions, Stillwell concludes that the rose hydroxide, which is the stable form, is the only crystalline modification of the hydroxide. The green and blue are considered to be amorphous precipitates, the green being the color by transmitted light and the blue being a reflected color—a Tyndall blue resulting from the scattering of light by the minute particles, the size of which is of the order of the wavelength of blue light.

Stillwell added $CoCl_2$ to KOH in amounts greater than 1 mol of the former to 1.5 mols of the latter and allowed the precipitate to age in the mother liquor. The color of the precipitate changed from green to blue to rose, the final product probably being a definite crystalline basic salt. Stillwell raised but did not settle the question as to whether the alleged basic salt was the same or different from Habermann's peach-blossom colored compound, $CoCl_2 \cdot 3CoO \cdot 3.5H_2O$[6] formed by adding ammonia to boiling cobaltous chloride.

Stillwell confirmed Benedict's[7] observation that small amounts of hydrous nickelous oxide or hydroxide precipitated with the cobalt hydroxide retard the change from blue to rose. Weiser[8] suggested that the specific stabilizing

[1] Ann., **13**, 155 (1835).

[2] Z. anorg. Chem., **73**, 304 (1912).

[3] "The Hydrous Oxides," 149 (1926).

[4] J. Phys. Chem., **33**, 1247 (1929).

[5] Z. anorg. Chem., **187**, 16 (1930).

[6] Monatshefte, 5, 432; J. Chem. Soc., **48** A, 351 (1885).

[7] J. Am. Chem. Soc., **26**, 695 (1904); cf. Test and Scoles: Proc. Indiana Acad. Sci., **34**, 163 (1924).

[8] "The Hydrous Oxides," 148 (1926).

action of the nickelous hydroxide on the blue cobaltous hydroxide is connected with the similarity in the crystalline structure of the two corresponding oxides. Stillwell accepts this in principle, but believes that both hydroxides are amorphous. "Hydrous nickelous oxide when freshly precipitated is laminar and amorphous and therefore stabilizes the laminar form of cobaltous hydroxide and inhibits crystal growth retarding the blue to rose change."

Thus Stillwell comes out definitely in support of the view that the difference in color between the blue or green compound on the one hand and the rose on the other, is due to isomerism, the former being the amorphous form and the latter the crystalline form of $Co(OH)_2$. In marked contrast to this point of view, Hüttig and Kassler[1] claim as a result of x-ray analysis of the blue and rose compounds, that both are crystalline, and have identical crystal structures. The difference in color is attributed to particle size alone, the blue being the more finely divided.

Five years ago[2] the hope was expressed that x-ray analysis methods would solve the question as to whether the difference in color between the blue is due to isomerism or to particle size. In view of the fact that two observers, working independently, reached opposite conclusions by these methods, it is obvious that a third independent series of observations is in order. The present paper purports (1) to study the stabilization of the blue cobaltous hydroxide, (2) to determine whether the color differences among the cobaltous hydroxides is due to isomerism, to particle size, or to both, (3) to formulate a mechanism for the transformation from blue to rose cobaltous hydroxide, and finally (4) to establish the nature and composition of the compound formed by ageing, in the mother liquor, the hydrous precipitate formed by the interaction of alkali with excess cobalt chloride.

Experimental

A. Stabilization of the Blue Hydroxide.

Blue cobaltous hydroxide usually passes over to the stable rose hydroxide in the presence of excess alkali. Hantzsch pointed out that this transformation is retarded by the presence of a slight excess of $CoCl_2$ and Benedict reported the stabilizing action of $Ni(OH)_2$ precipitated simultaneously. Hantzsch showed that the excess $CoCl_2$ was adsorbed. This was confirmed by Stillwell who attributed the stabilizing action to the inhibition of crystal growth by the adsorbed salt. The stabilizing action of nickelous hydroxide was attributed to a similar cause. The presence of the sulfates of ferrous iron, zinc, manganese, magnesium, chromium, copper, and aluminum; and the nitrates of lead, cadmium, thorium, and strontium are said by Chatterji and Dhar[3] to have little or no stabilizing effect.

Since the stabilization is the result of adsorption it seems altogether unlikely that only the salts of cobalt and nickelous hydroxide should have a

[1] Z. anorg. Chem., **187**, 16 (1930).
[2] "The Hydrous Oxides," 149 (1926).
[3] Chem. News, **121**, 253 (1920).

stabilizing action on the blue to rose transformation. Actually a number of substances were found not only to retard but actually to stop the change. The results of these observations will be given in the following paragraphs.

Effect of Cobaltous Chloride. For the sake of comparison, observations were made of the color changes which take place in the $Co(OH)_2$ precipitated in the presence of an excess of $CoCl_2$. Approximately 0.5 gram of $Co(OH)_2$ was precipitated by mixing solutions as indicated in Table I in an apparatus designed for rapid uniform mixing of solutions.[1]

TABLE I

Effect of $CoCl_2$ on the Stability of Blue $Co(OH)_2$
2M NaOH, 5 cc; total volume, 25 cc)

M CoCl₂		Color after			
cc	5 sec.	5 min.	1 day	3 days	8 days
5	blue	some rose	rose	rose	rose
6	blue	light blue	light blue	light blue	green blue
7	blue	green	green	green	green
8	blue	green	green	green	light blue
9	blue	green	green	green	lavender
10	blue	green	green	light blue	lavender
11	blue	green	light blue	lavender	lavender
12	blue	some green	light blue	lavender	lavender
13	blue	dark blue	light blue	lavender	lavender
14	blue	dark blue	some lavender	lavender	lavender
15	blue	dark blue	some lavender	lavender	lavender

Similar experiments carried out with air-free solutions and kept out of contact with the air gave identical results. For corresponding conditions the color changes were essentially the same as those reported by Stillwell. The formation of a green hydroxide in the absence of air disproves Winkelblech's conclusion that the green color necessarily results from oxidation. Stillwell showed, however, that a green coloration is obtained by partial oxidation of the blue compound.

Effect of Mannitol. Since cane sugar is apparently adsorbed by the hydrous oxides of copper[2] and iron[3] it was suggested that certain carbohydrates and higher polyhydroxy alcohols might retard the transformation of the unstable blue to the rose cobaltous hydroxide. That such is the case is shown by the following results. Using the same procedure as in the previous experiment, varying amounts of mannitol were added to the reaction mixture previous to precipitation. The observations with $CoCl_2$ in excess and with NaOH in excess are given in Tables II and III, respectively.

[1] Weiser and Middleton: J. Phys. Chem., **24**, 48 (1920).
[2] Graham: Phil. Trans., **152**, 283 (1861).
[3] Riffard: J. Chem. Soc., **27**, 292 (1874).

TABLE II

Effect of Mannitol on the Stability of Blue Co(OH)$_2$ in the Presence of Excess CoCl$_2$

(M CoCl$_2$, 6 cc; 2 M NaOH, 5 cc; total volume, 25 cc)

M Mannitol cc	Color after				
	5 seconds	5 minutes	1 hour	1 day	10 days
0.0	blue	light blue	blue-green	light green	green
0.1	blue	dark green	green	green	green
0.25	blue	dark green	green	green	green
0.5	blue	dark green	green	green	green
1.0	blue	dark green	green	green	green
2.0	blue	dark green	green	green	green
3.0	blue	dark green	green	green	green
9.0	blue	dark green	green	green	green

TABLE III

Effect of Mannitol on the Stability of Blue Co(OH)$_2$ in the Presence of Excess NaOH

(M CoCl$_2$, 4 cc; 2 M NaOH, 6 cc; total volume 25 cc)

M Mannitol cc	Mol ratio Mannitol : Co	Color at start	Observations
0.001	0.00025	blue	rose in 10 minutes
0.01	0.0025	blue	rose in 12 minutes
0.1	0.025	blue	rose in 18 minutes
0.2	0.05	blue	still some blue after 4 weeks
0.5	0.125	blue	no change in 4 weeks
1.0	0.25	blue	no change in 4 weeks
2.0	0.5	blue	no change in 4 weeks
3.0	0.75	blue	no change in 4 weeks
4.0	1.0	blue	no change in 4 weeks
5.0	1.25	blue	no change in 4 weeks

It is clear from these observations that a very small amount of mannitol will completely inhibit the transformation from blue to rose Co(OH)$_2$ even in the presence of an excess of NaOH, which ordinarily favors a rapid change.

All of these observations were made at room temperature. To determine the stabilizing effect at higher temperatures the sample prepared as in Table III containing 2 cc of M mannitol was heated on a water bath at 92° for 8 hours. No noticeable change in color was observed.

Effect of Several Sugars, etc. The influence of a number of sugars, polyhydroxy alcohols, gelatin, etc. on the blue to rose transformation have been summarized in Table IV.

TABLE IV

Effect of Several Substances on the Stability of Blue Co(OH)₂ in the Presence
of Excess NaOH

(M CoCl₂, 4 cc; 2 M NaOH, 6 cc; total volume, 25 cc)

Stabilizer added (0.1g.)	Color after 2 weeks
Maltose	Original deep blue
Lactose	Original deep blue
Xylose	Original deep blue
Arabinose	Original deep blue
Sucrose	Original deep blue
Galactose	Original deep blue
Dextrose	Original deep blue
Dulcitol	Original deep blue
Sorbitol	Light blue
Raffinose	Original deep blue
Glucose penta-acetate	Light blue, some rose
Egg albumin	Some rose by the end of 1 hour
Gelatin	Mostly rose by the end of 1 hour
NiCl₂	Mostly rose by the end of 1 hour

Effect of Potassium Sulfate. Hantzsch observed that the blue precipitate
formed in the presence of a small excess of $CoSO_4$ was more stable than that
formed in the presence of $CoCl_2$, probably because of stronger adsorption of
the sulfate than of the corresponding chloride. This suggests that the addi-
tion of sulfates might retard the blue to rose transformation, even in the
presence of excess alkali. This was tested out with the results shown in
Table V. It is obvious that the salt retards distinctly the blue to rose trans-

TABLE V

Effect of K_2SO_4 on the Stability of Blue Co(OH)₂

Solutions mixed				Color after				
2M KOH cc	M CoCl₂ cc	H₂O cc	Satd. K₂SO₄ cc	5 sec.	10 min.	30 min.	16 hrs.	24 hrs.
5	4	11	0	blue	rose	rose	rose	rose
5	4	0	11	blue	blue	light blue	some rose	rose

formation when present in large excess. That the retarding effect is not
more marked as compared with $CoSO_4$ is probably due to very much weaker
adsorption of K_2SO_4 than of $CoSO_4$.

B. Adsorption of Sugars by Co(OH)₂.

Since the sugars exhibit such a marked stabilizing effect on the blue
$Co(OH)_2$ even when present in low concentration, it would follow that the
sugars should be strongly adsorbed. The following experiments show that
this is the case:

In a 100 cc flask were placed amounts of CoCl$_2$ and sugar solutions as listed in Table VI; then 11 cc of NaOH was added; and finally more water to the 100 cc mark on the flask.   The contents of the flask were shaken thoroughly for a few minutes and then centrifuged. A portion of the supernatant solution was withdrawn and analyzed for sugar.

The analysis of sugars were made with a Reichert Soleil-Ventzke saccharimeter.   The following normal weights were used: 100 Ventzke degrees equivalent to 26.00 grams of sucrose; 32.857 grams of lactose; 12.474 grams of maltose; and 16.507 grams of raffinose.[1] No attempt was made to use a different normal weight for different parts of the scale as the correction is small.   Thus at 5 Ventzke degrees, the normal weight of sucrose is given as 24.90 grams.   Temperature corrections were made.

<div align="center">

TABLE VI

Adsorption of Sugars by Blue Co(OH)$_2$

</div>

[Solutions mixed (total volume 100 cc): 10 cc 0.9947 M CoCl$_2$ equivalent to 0.9247 g Co(OH)$_2$; 11 cc 2.23 M NaOH (excess NaOH 0.045 M); sugar solutions as listed below]

Sugar cc	Concentration in mols/liter		Adsorption in mols sugar/mol Co(OH)$_2$
Sucrose 0.9899 M	Initial	Final	
5.00	0.0495	0.0351	0.145
10.00	0.0990	0.0736	0.255
20.00	0.1980	0.1566	0.415
Lactose 0.3115 M			
10.00	0.0312	0.0160	0.159
20.00	0.0623	0.0323	0.302
40.05	0.1248	0.0758	0.493
50.00	0.1557	0.0986	0.574
Maltose 0.1201 M			
20.00	0.0240	0.0138	0.103
70.00	0.0841	0.0627	0.215
Maltose 0.2572 M			
20.00[2]	0.0514	0.0358	0.157
50.00[2]	0.1286	0.1067	0.220
Raffinose 0.1386 M			
20.00	0.0277	0.0232	0.0452
70.00	0.0970	0.0833	0.138

[1] International Critical Tables, **2**, 335 (1924).

[2] In these experiments 20.00 cc of 0.4980 M CoCl$_2$ were used.

The effect of the excess NaOH and NaCl on the solution was determined and found to be negligible for the purposes of these experiments. Thus 25 cc of a 0.9899 molar sucrose solution diluted to 100 cc gave a saccharimeter reading of 32.36 Ventzke degrees. In the presence of the same amounts of NaOH and NaCl as in the adsorption experiments, the reading was 31.77 degrees. This difference of 0.59 degree corresponds to 0.004 mol of sucrose
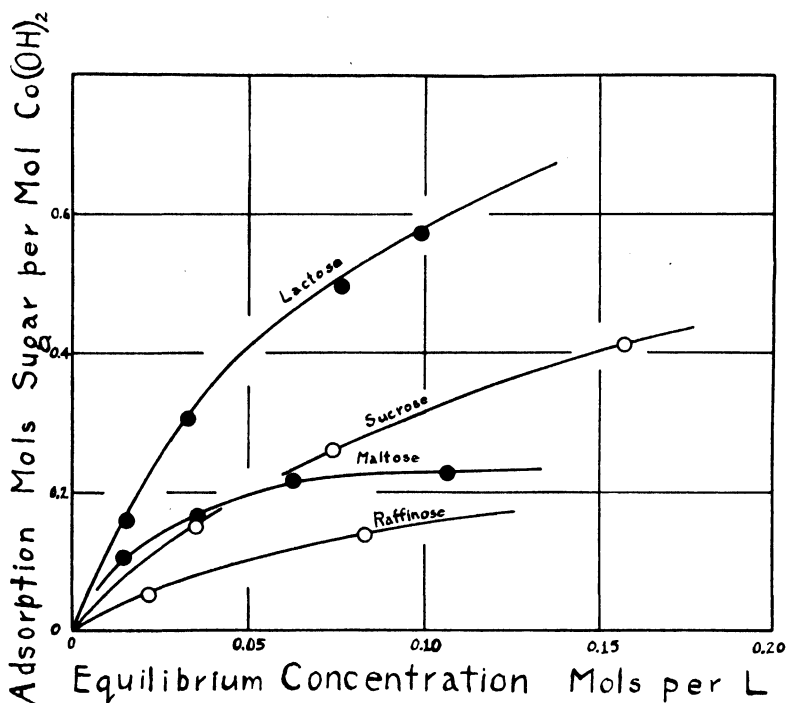
FIG. 1
Adsorption of Sugars by Blue Co(OH)$_2$.

per liter or to an adsorption of approximately 0.004 mol sucrose per mol Co(OH)$_2$.

The adsorption data are given in Table VI and are shown graphically in Fig. 1. It will be noted that typical adsorption isotherms are obtained in each case. All the sugars are strongly adsorbed, even at relatively low concentrations. The order of adsorption is: lactose > maltose > sucrose > raffinose.

C. X-Ray Analysis of Cobalt Hydroxides.

Before considering the mechanism of the transformation from the blue to rose cobaltous hydroxide and the inhibiting of this process by adsorbed substances, it seems advisable to report the results of x-ray analysis of the several preparations. X-ray diffraction patterns were obtained by the powder method using a General Electric Diffraction Apparatus. The following preparations were examined:

1. Rose Co(OH)₂. The sample was precipitated in the cold with excess NaOH and allowed to stand for 15 minutes until the transformation from blue to rose was complete. After washing with water by the aid of the centrifuge until peptization started,[1] it was washed once with alcohol, dried at 60° and ground in an agate mortar. There was no indication of any oxidation. The x-ray pattern was obtained at once.

2. Blue Co(OH)₂, dried. The sample was precipitated in the presence of a slight excess of CoCl₂ and was washed at once and dried like 1. After grinding, the color was a blue-gray. It was probably oxidized slightly. It stood over CaCl₂ for 5 months before its diffraction pattern was made.

3. Green Co(OH)₂, dried. The sample was prepared and treated exactly as 2 except that a larger excess of CoCl₂ was present during the precipitation. It was decidedly green in color.

4. Blue Co(OH)₂, moist, not stabilized. This sample was prepared like 2, except it was not washed or dried. Some rose was visible at the end of the x-ray exposure.

5. Blue Co(OH)₂, moist, stabilized. This sample was prepared as described in Table III, using 0.2 cc of mannitol solution as a stabilizer. It was sealed in a glass tube without washing or drying and the x-radiogram made. The preparation still possessed the original blue color after one month.

TABLE VII

X-Ray Diffraction Data for the Rose, Blue, and Green Co(OH)₂

1. Rose 9 hours		2. Blue (dry) 8 hours		3. Green (dry) 8 hours		4. Blue (moist) 8 hours		5. Blue (moist and stabilized) 20 hours	
d/n Å	I	d/n Å	I	d/n Å	I	d/n Å	I	d/n Å	I
4.66	8	4.66	6	3.93	8	4.66	2	5.6	8
2.75	5	4.00	6	2.63	10	4.00	2	3.99	8
2.37	10	2.66	10	1.536	1	2.66	3	2.63	10
1.780	8	2.37	4	1.315	0.5	2.34	10	1.536	5
1.590	6	1.785	0.5			1.752	4	1.459	0.1
1.504	4	1.555	0.6			1.574	3	1.215	0.1
1.350	1	1.316	0.1					1.000	0.1
1.318	3							0.937	0.1
1.183	2								
1.140	0.1								
1.108	0.5								
1.068	0.1								
1.014	0.1								
0.948	0.1								
0.918	0.1								

[1] Cf. Tower and Cook: J. Phys. Chem., **26**, 728 (1922).

The planar spacings were read off the several x-radiograms and the intensities (I) were estimated visually on such a scale that 10 means the most intense line, and 0.1 means a line that is just visible. These results are tabulated in Table VII and given in chart form in Fig. 2. The time noted in the table is the time of exposure to the x-rays in making the x-radiogram.

From the observed data there appears to be no doubt that blue $Co(OH)_2$ exists in a crystalline form different from rose $Co(OH)_2$. It will be noted
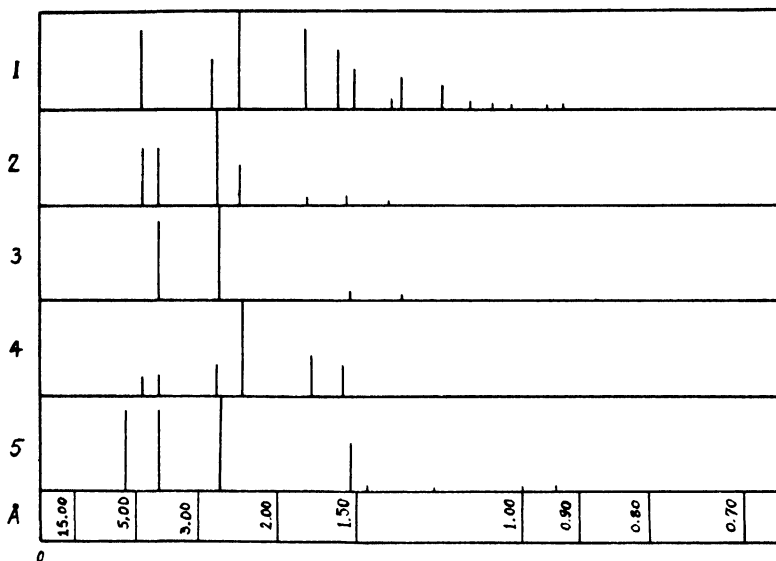
FIG. 2

Diagram of the X-radiograms of Cobaltous Hydroxides. (1) Rose; (2) Blue (dry); (3) Green (dry); (4) Blue (moist); (5) Blue (stabilized). Samples contain some Rose.

that the dried blue and green samples (2 and 3) all have the same planar spacings except for some lines which correspond to the rose preparation, 1. It would be expected that these samples would contain some rose. Some rose was visible in sample 4 at the end of the x-ray exposure. However, the moist blue sample, stabilized with mannitol, retains its original deep blue color and is probably free from any of the rose form. The latter sample contains NaCl, NaOH, and a small amount of mannitol, but these are in solution and therefore do not influence the x-ray pattern. A comparison of the diffraction pattern for the stabilized blue hydroxide, with those for samples 2, 3, and 4, discloses that the spacings are nearly identical for all samples after the lines in 2, 3, and 4 belonging to the rose, are cancelled off.

These observations not only show the existence of two crystalline forms of $Co(OH)_2$ but disclose that the blue and green samples are identical in crystal structure. The results appear to disprove Stillwell's[1] conclusion that the blue and green precipitates are amorphous. The similarity in crystal structure between the blue and green preparations supports Stillwell's view

[1] J. Phys. Chem., 33, 1247 (1929).

that this color difference is not due to isomerism. His claim that the green is the color by transmitted light, and the blue is a Tyndall blue, is probably correct.

Hüttig and Kassler[1] were correct in concluding that both the blue and the rose hydroxides are crystalline. They were altogether wrong however, in their deduction that the two are identical in crystal structure, and the difference in color is due to particle size. It is probable that the blue sample which they examined with the x-rays contained so much rose that they completely overlooked the fainter lines belonging to the blue form.

The Mechanism of the Blue to Rose Transformation and the Stabilization of the Blue Hydroxide.

In view of the marked adsorption of certain sugars by blue $Co(OH)_2$ and the marked retarding action of relatively small amounts of the sugars, there is little doubt but that the two phenomena bear to each other the relation of cause and effect. It will be recalled that the order of adsorption of the sugars investigated is: lactose > maltose > sucrose > raffinose. It is of interest to note that the peptizing action of sugars, as a result of adsorption, on hydrous ferric oxide[2] follows the same order. A similar peptizing action of the adsorbed sugars on the blue $Co(OH)_2$ was noted. In some cases the sol formed originally was thrown down completely only after centrifuging for an hour at 3000 r.p.m.

The probable mechanism of the transformation of the blue to rose hydroxide consists in the solution of the minute blue crystals in the excess alkali followed by reprecipitation of the less soluble, larger, rhombic crystals of the rose isomer. The addition of strongly adsorbed substances such as mannitol, various sugars, etc., surrounds the blue particles with a protective layer which inhibits or prevents the isomeric transformation. In the presence of excess cobalt salt, the isomeric transformation is prevented not only by strong adsorption of the salt but by the tendency to form a basic salt as described in the next section. In the absence of alkali, the solvent action of the mother liquor is insufficient to bring about the isomeric change, even at temperatures considerably above room temperature; on the other hand, in the presence of alkali, without the presence of a stabilizing substance, the transformation is quite rapid at higher temperatures.

D. Basic Cobalt Chloride.

As already noted in Table I, the aged precipitate formed by adding excess $CoCl_2$ to sodium hydroxide solution varies in color from green to blue to rose (lavender) depending on the age and the excess amount of $CoCl_2$ in the mother liquor. This confirms the observations of Stillwell. X-ray diffraction patterns were made of the following preparations:

1. Aged Green-Blue. To 5 cc of 2 M NaOH solution was added 6 cc of 1 M $CoCl_2$ solution. After eight days, the green-blue precipitate was removed from the mother liquor by centrifuging, but was neither washed nor dried.

[1] Z. anorg. Chem., **187**, 16 (1930).

[2] Dumanski, et al: Kolloid-Z., **51**, 210 (1930); **54**, 73 (1931); J. Russ. Phys.-Chem. Soc., **62**, 722 (1930).

2. Aged Green. This was prepared in the same way as the preceding sample, except that 7 cc of $CoCl_2$ was used.

3. Aged Rose (Lavender). This precipitate was prepared and aged in the same way as the two preceding ones, except that 15 cc of $CoCl_2$ was used. Stillwell calls this material "aged rose"; it is, however, more of a bluish-rose which we have designated as lavender.

4. Lavender, Dried. The precipitate prepared as number 3 was washed with water by the aid of the centrifuge until a sol began to form and finally with alcohol. It was dried at 60°.

The planar spacings and the intensities of the lines of the several preparations are given in Table VIII and shown diagrammatically in Fig. 3.

TABLE VIII

X-Ray Diffraction Data for the Green, Blue, and Lavender Aged Precipitates

1. Blue-Green (moist) 18 hours		2. Green (moist) 18 hours		3. Lavender (moist) 18 hours		4. Lavender (dry) 8 hours	
d/n Å	I	d/n Å	I	d/n Å	I	d/n Å	I
4.66	7.0	5.6	5.0	5.6	8.0	5.5	8.0
4.00	6.0	4.6	5.0	2.69	9.0	2.77	6.0
2.74	9.0	4.01	4.0	2.30	10.0	2.28	10.0
2.68	9.0	2.69	10.0	2.07	1.0	2.14	0.1
2.37	10.0	2.37	6.0	1.96	2.0	1.948	0.1
2.00	3.0	2.00	4.0	1.831	3.0	1.820	3.0
1.775	5.0	1.806	0.1	1.711	5.0	1.701	0.1
1.695	0.2	1.707	0.2	1.613	2.0	1.610	0.2
1.575	4.0	1.574	4.0	1.536	3.0	1.535	0.2
1.531	3.0	1.533	4.0	1.458	3.0	1.513	0.1
1.498	3.0	1.491	0.1	1.391	0.5	1.390	0.1
1.344	1.0	1.453	0.1	1.367	2.0	1.367	0.1
1.313	2.0	1.350	2.0	1.286	1.0	1.285	0.1
1.229	0.1	1.310	2.0	1.247	1.0	1.248	0.1
1.178	0.1	1.230	0.1	1.208	0.5	1.134	0.1
1.086	0.2	1.176	0.1	1.167	0.1	1.103	0.1
1.023	0.1	1.084	0.1	1.136	0.5	1.062	0.1
1.009	0.1	1.024	0.2	1.107	0.3		
0.940	0.1	1.003	0.1	1.066	0.1	more very faint	
0.898	0.1			1.028	0.1	lines present	
0.752	0.1			0.986	0.1		
0.718	0.1			0.947	0.1		
				0.929	0.1		
				0.883	0.1		
				0.839	0.1		
				0.796	0.1		
				0.756	0.1		

A comparison of the above diffraction data with those for the blue, and the rose hydroxides, Table VII, discloses that the lavender precipitate is a different compound, probably a basic salt as suggested by Stillwell.   To determine whether this was the case or whether it was a third isomeric form of Co(OH)₂, the carefully prepared, washed, and dried sample (4 above) was analyzed for cobalt and chloride.   The cobalt was determined by electrodeposition of the metal and the chloride was estimated as AgCl.   The data are given in Table IX.
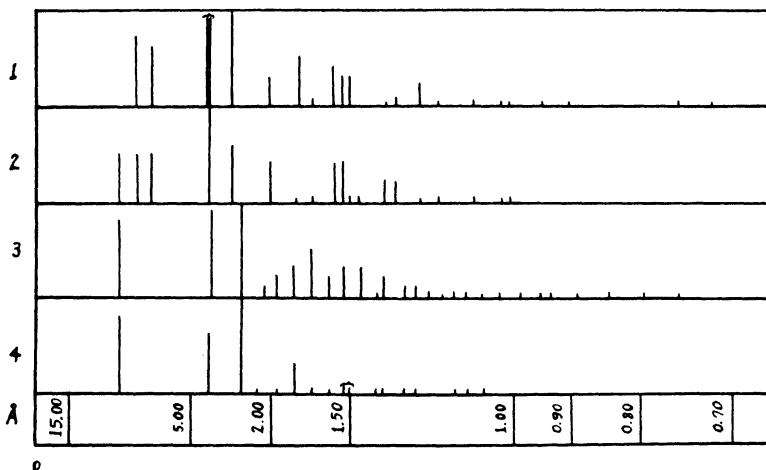
FIG. 3

Diagram of the X-radiograms of Precipitates formed by ageing Co(OH)₂ in CoCl₂ Solution. (1) Green Blue; (2) Green; (3) Lavender (moist); (4) Lavender (dried).   The Lavender Precipitates are chiefly the Basic Salt, CoCl₂·3CoO·3.5 H₂O.

TABLE IX

Analysis of the Basic Cobalt Chloride

Sample g	Co g	AgCl g	Percent			
			Found		Calculated for CoCl₂·3CoO·3.5H₂O	
			Co	Cl	Co	Cl
0.2990	0.1687		56.42		56.44	
0.1162		0.0788		16.8		16.98

The results show that a definite, crystalline, basic salt is formed, the composition of which corresponds to Habermann's basic cobalt chloride, CoCl₂·3CoO·3.5H₂O, formed by the action of ammonia on a hot solution of CoCl₂.

Summary

The conclusions to be drawn from this investigation may be summarized as follows:

    1. Cobaltous hydroxide Co(OH)₂ exists in two isomeric crystalline forms as evidenced by x-ray analysis.

2. Cobaltous hydroxide may be blue, green, or rose in color. The green and blue preparations, α Co(OH)$_2$, are identical in crystalline structure, while the rose, β Co(OH)$_2$, is distinctly different.

3. Conclusions 1 and 2 are contrary to those of Stillwell who believed that the blue and green hydroxides are amorphous, and to those of Hüttig and Kassler who believed that the blue and rose are identical in crystal structure, the difference being due to variation in particle size. It is probable that the blue sample subjected to x-ray analysis by Hüttig and Kassler contained so much rose that the fainter lines belonging to the blue form were completely overlooked.

4. The blue and green preparations owe their difference in color to a difference in physical character. The green is the color by transmitted light and the blue is probably a reflected color, a Tyndall blue (Stillwell).

5. α Co(OH)$_2$ is the instable form. In the presence of alkali it dissolves and reprecipitates in the less soluble, stable β modification.

6. The α to β transformation can be prevented or retarded by the presence of strongly adsorbed substances in the solution from which the α form precipitates. The blue form is stabilized indefinitely by small amounts of mannitol, sorbitol, dulcitol, sucrose, lactose, maltose, xylose, arabinose, raffinose, galactose, and dextrose. The transformation is retarded by cobalt salts (Hantzsch), Ni(OH)$_2$ simultaneously precipitated (Benedict), albumin, gelatin and sulfates.

7. Adsorption isotherms of various sugars with Co(OH)$_2$ as adsorbent are given. The adsorption is strong even in relatively low concentrations, as would be expected from the marked stabilizing action of the compounds. The order of adsorption is: lactose > maltose > sucrose > raffinose. The peptizing action of the sugars as a result of adsorption on hydrous ferric oxide (Dumanski) follows the same order.

8. Cobaltous hydroxide in contact with a solution of CoCl$_2$ undergoes color transformations from green to blue to lavender. The blue and green substances are mixtures of α Co(OH)$_2$, β Co(OH)$_2$, and a basic salt CoCl$_2$·3CoO·3.5H$_2$O. The lavender compound formed on long standing is the pure basic salt.

9. The color transformations and the composition of the various colored substances formed by the interaction of alkali and CoCl$_2$ may be represented as follows:

α Co(OH)$_2$ Excess CoCl$_2$ α Co(OH)$_2$ Excess alkali β Co(OH)$_2$
β Co(OH)$_2$ $\longleftarrow$ Blue, Green $\longrightarrow$ Rose
    CoCl$_2$·3CoO·3.5H$_2$O
        Green
            $\downarrow$
    α Co(OH)$_2$
    β Co(OH)$_2$ $\longrightarrow$ CoCl$_2$·3CoO·3.5H$_2$O
        CoCl$_2$·3CoO·3.5H$_2$O   Lavender
            Blue

The Rice Institute,
Houston, Texas.
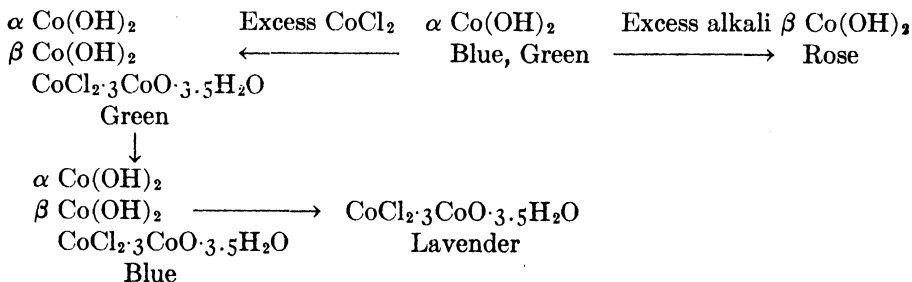
THE INFLUENCE OF GASES ON THE STABILITY
OF ZSIGMONDY GOLD SOLS

BY WM. H. CONE, H. V. TARTAR AND T. IVAN TAYLOR

It is generally believed that metal sols owe their stability to the preferential adsorption of ions from an electrolyte, which produces a potential difference at the interface between the metal and the dispersion medium. If this potential is reduced below a certain critical value the colloidal particles adhere to form larger aggregates and coagulation takes place.

Recent work in this laboratory[1] indicates that adsorption potentials of platinum and gold electrodes in certain electrolytes are markedly influenced by the presence of gases in solution, particularly oxygen. Frumkin and his coworkers[2] have also shown that the presence of hydrogen and oxygen modify the adsorption of electrolytes by platinum and platinized activated charcoal.

The work presented in this paper is a series of experiments on the effect of gases on the coagulation and the cataphoresis of Zsigmondy gold sols. The investigation was undertaken in the hope that the data might add some knowledge concerning the effect of dissolved gases on adsorption. Questions like the following naturally arise: is there a change in potential (zeta potential) between the particles and the solution; does a chemical change take place at the interface; is the change only physical in nature? It was found that air, oxygen, nitrogen and especially hydrogen have a stabilizing effect.

Experimental Part

(a) *Preparation of materials.* The gold sols were prepared essentially according to the directions given by Zsigmondy.[3] In some cases the concentration of the gold was varied as much as 50 percent. The procedure for reducing the gold must be carefully followed in detail in order to secure satisfactory results. The writers have confirmed the results of Faraday[4] and of Zsigmondy[5] that two primary precautions in the preparation of a finely dispersed gold sol are the purity of the water and the cleanliness of the glassware. "Conductivity water" with specific conductance of 2×10^{-6} or less was used. Great care was taken to have the pyrex glass vessels physically and chemically clean. A fresh sol was prepared for each experiment and no special attempt was made to obtain sols of very uniform concentration and appearance.

[1] Tartar and McClain: J. Am. Chem. Soc., **53**, 3201 (1931).

[2] Frumkin and Obrutschewa: Z. anorg. Chem., **168**, 84-6 (1926); Frumkin and Donde: Ber., **60B**, 1816 (1927).

[3] Zsigmondy: Z. anal. Chem., **40**, 687 (1901).

[4] Faraday: Phil. Trans., **147**, 145 (1857).

[5] Zsigmondy: Z. anal. Chem., **40**, 697 (1901).

A 0.2 M solution of sodium chloride was prepared for use as a precipitating agent. The sodium chloride was of "C. P. analyzed" quality and was further purified by recrystallization.

(b) *Method of Procedure.* The sols were put in 150 cc. pyrex flasks which had been fitted with tubes and stoppers to permit the bubbling of gas through the contents. A flask of water was connected in series so that the gas was bubbled through water before going into the sol in order to prevent undue evaporation from the latter. One flask was completely filled with sol and tightly stoppered to serve as a blank for comparison. The gases were bubbled through the sols for a number of hours until they were saturated. It was found that after passing gas through a sol for two hours, further passing of the gas did not affect the results. The precipitation was carried out by transferring 10 cc. of the sol into a test tube and adding from another test tube a measured volume of the sodium chloride solution which had been diluted with water to 15 cc. This sodium chloride solution was saturated with the gas. Experiment showed, however, that there was no apparent difference in the results where the precipitating solution was not saturated with gas. The mixing was accomplished by pouring back and forth from one test tube to the other six times. Varying amounts of sodium chloride were used until a concentration was found which would produce a change in color from red to blue in approximately two minutes and give complete precipitation in about twelve hours.

In the beginning experiments the saturation with gas and precipitation was carried out at 25°. It was found, however, that change of temperature did not exert any marked effect and consequently some of the later experiments were made at room temperature.

In order to show that the effects of the gas were not due to mechanical agitation by bubbles, a number of sols were placed in strong pyrex flasks

TABLE I

Stabilizing Effect of Gases on the Precipitation Value of Gold Sols

No. of gold sol	Hydrogen 3 Atmos. Press.	Hydrogen Atmos. Press.	Air	Nitrogen	Oxygen	Blank
1	—	—	—	103	—	64
2	—	64	—	40	—	32
3	—	40	—	—	—	32
4	—	40	—	—	—	32
5	—	40	24	—	—	12
6	—	68	48	—	40	32
7	—	48	40	—	36	28
8	48	24	—	—	—	16
9	28	28	—	—	—	28
10	48	24	12.5	—	12.5	6
11	48	48	—	—	—	48
12	—	32	—	—	—	20

and subjected to hydrogen under a pressure of three atmospheres without agitation for three to four hours. The pressure was then released and the sol precipitated as described above.

(c) *Results and Discussion of Precipitation Experiments.* The data from the precipitation experiments are given in Table I. The numerical values represent the concentration of sodium chloride in millimols per liter necessary to produce precipitation.

These data show, in general, that hydrogen, air, nitrogen and oxygen all had a stabilizing effect, hydrogen having a more pronounced effect than the other gases. All the sols gave a higher precipitation value after saturation with a gas than the blanks, except sols 9 and 11. Number 9 was a very dilute sol and had an exceptionally bright red, clear appearance. Number 11 was originally a somewhat cloudy, unstable sol which was allowed to stand for some time and most of the gold had precipitated leaving a very clear, dilute sol. With the other sols the presence of the gas, whether bubbled or under pressure, produced a marked change in appearance; they became brighter red and lost some of the turbid appearance by reflected light. This color change was most noticeable when hydrogen was used. According to Zsigmondy[1] a gold sol consisting of primary particles is red and the changes in color during the process of coagulation are due to aggregation of these primary particles. Our results indicate therefore that when the sols were subjected to gases the secondary or aggregated particles became more highly dispersed thus giving a color change toward the red and an increase in the stability of the sol. This opinion is supported by the results with sols 9 and 11 the appearance of which indicated the presence of very few, if any, secondary particles.

The effects reported in Table I cannot be ascribed to the influence of the electrolyte used in the preparation of the sol. A limited number of experiments in this laboratory by E. E. Hardinger show that the gases exert a marked effect upon the precipitation values of gold, silver, palladium and platinum sols prepared by the Bredig arc method.

The precipitation values of sols 3 and 4, Table I, were determined after being saturated with air and with hydrogen and then the gases were changed so that air was bubbled through the one saturated with hydrogen and hydrogen through one saturated with air. The air had no effect on the precipitation value of the sol previously saturated with hydrogen even after bubbling as much as 50 hours, but the one originally saturated with air soon became as stable as the hydrogen-saturated sol. This finding is quite the opposite of the results obtained by Pennycuick[2] on platinum sols prepared by the Bredig method.

The writers believe that the effect of the gases on the gold sols is due to adsorption rather than to chemical combination. The ineffectiveness of air on a sol previously saturated with hydrogen and the ease with which the sol saturated with air may be changed with hydrogen, seem to support this view. At least, no case of easily reversible oxidation and reduction obtains. Both

[1] Zsigmondy: "Kolloidchemie," 4th Edition, p. 67.

[2] Pennycuick: J. Am. Chem. Soc., **52**, 4622 (1930).

hydrogen and oxygen seem to exert an influence in the same direction. It is well known, too, that hydrogen is strongly adsorbed by platinum and cannot be easily removed.

(d) *Cataphoresis experiments.* Careful experiments were made to determine the influence of hydrogen on the cataphoresis of gold particles. It was hoped that these experiments would afford positive evidence that this gas influences the potential difference between the micelle and the solution.

The measurements were made by the Burton method as modified by Kruyt and van der Willigen.[1] The liquid in contact with the colloid was obtained by ultrafiltration of the sol through a collodion filter. The velocities were calculated from the formula

$$\mu = \frac{\frac{1}{2}(W_1 + W_2)H}{T\ E}$$

where μ is the velocity in microns per second per volt centimeter, W_1 and W_2 are the observed distances the rising and falling interfaces move respectively, H is the distance in centimeters between the electrodes, T is the time in seconds and E is the applied potential. The data are presented in Table II.

TABLE II

Cataphoretic Velocities of Gold Particles
with and without Hydrogen

Sol No.	Gas Bubbled	Time min.	Cm. between electrodes	Volts	Displacement left mm.	Displacement right mm.	Veloc. in μ at 25°
12	None	15	21.12	70	10.7	11.0	3.63
12	H$_2$	15	21.12	70	10.7	11.3	3.68
13	None	15	21.01	70	11.0	10.2	3.54
13	None	15	21.18	70	10.5	11.0	3.60
13	H$_2$	15	21.34	70	10.9	10.1	3.56

The results show no change in the velocity of the gold particles after they have been treated with hydrogen gas. The interpretation of this finding is difficult. The potential difference between the disperse phase and the dispersion medium is evidently due to a layer of sparsely distributed mobile ions which may be many molecular diameters in thickness.[2] For this reason usual calculations of potential differences from cataphoretic data have a fictitious significance. A change in potential difference should, however, be shown by the cataphoretic velocity unless there might be some compensating effects such as change of thickness of the adsorbed ionic film and the potential gradient.

[1] Kolloid-Z., **44**, 22 (1928).

[2] McBain: J. Phys. Chem. **28**, 706 (1924); Burton: Colloid Symposium Monograph, **4**, 132 (1926); Tartar and McClain: J. Am. Chem. Soc., **53**, 3201 (1931).

A possible explanation of the results of Tables I and II is that the presence of the gases modifies the adsorption of the ions of the precipitating electrolyte. If this be true, then varying amounts of electrolyte would be required for precipitation depending on the kind of gas used.

Summary

1. Zsigmondy gold sols which have a brownish turbid appearance have a much higher precipitation value after being saturated with a gas, especially with hydrogen. There is also a marked change in color during saturation.

2. Zsigmondy gold sols which are very clear and dilute do not show a higher precipitation value nor is there any color change during saturation.

3. The changes can hardly be attributed to any oxidation or reduction action for both hydrogen and oxygen exert an influence in the same direction.

4. Cataphoresis experiments do not indicate a change of potential difference between the micelle and the dispersion medium when the sol is saturated with hydrogen.

THE AUTOXIDATION OF STANNOUS AND
CUPROUS CHLORIDES BY AIR

BY GEORGE W. FILSON AND JAMES H. WALTON

The oxidation of solutions of stannous chloride was first studied extensively by Young[1] who found that the reaction was somewhat dependent upon the acidity of the solution, highly sensitive to the action of certain catalysts such as copper and iron salts, and further, was inhibited by some of the alkaloids and certain other substances. The reaction was also studied by Miyamoto,[2] who determined the effect of acid concentration, the rate of bubbling of the oxygen, and several other factors.

It has been shown by many investigators that autoxidations are catalyzed by the presence of certain metallic ions, notably by those of copper, iron, manganese, cobalt, and nickel. This investigation was originally undertaken with the object of finding out whether or not a mixture of these ions exhibit promoter action in the case of autoxidations. Since no cases of promoter action were found, certain physical and chemical conditions affecting the autoxidation of stannous and cuprous chlorides have been studied.

Reagents: In most cases no special precautions were taken to further purify the reagents inasmuch as very pure reagents were available. The stock solutions of stannous chloride were made by dissolving a weighed amount of the salt in air-free distilled water containing enough hydrochloric acid to prevent the precipitation of any of the basic chlorides of tin. These solutions were kept under an atmosphere of hydrogen.

Apparatus: The apparatus used in these experiments was essentially the same as that used by Walton.[3] This apparatus consists of a burette and leveling tube connected to a reaction flask by means of capillary glass tubing. The reaction flask was clamped in a vertical position and by means of an appropriate mechanism, it was rotated back and forth around the vertical axis. The only deviation from the original apparatus was in the shape of the reaction flask (Fig. 1). The bottom of a 150 cc. round bottom Pyrex flask was heated in such a way that a narrow band, extending to within an inch of the end of the neck on either side and parallel to the vertical axis, was softened. This softened portion was then pressed in by the edge of an iron spatula so that a fissure about one-half inch deep was formed. A second fissure was made in a plane at right angles to the first. When shaken, the ridge on the inside of the flask breaks the surface of the liquid and in this way drives the liquid into the gaseous phase and drives the gas into the liquid phase.

Method of Procedure: The concentration of acid in the stannous chloride solution was determined by titration of a measured sample with standard

[1] Young: J. Am. Chem. Soc., **23**, 119 (1910).
[2] Miyamoto: Bull. Soc. Chem., Japan, **2**, 155 (1927) et. seq.
[3] Walton: Z. physik. Chem., **47**, 185 (1904).

sodium hydroxide. This gives the sum of the free hydrochloric acid and the acid that would be formed upon the complete hydrolysis of the stannous chloride or its basic salts. In determining the rate of oxidation of the stannous chloride, a given quantity (25 cc. unless otherwise noted) of the stock solution of stannous chloride was placed in the reaction flask which was then clamped into position and connected to a burette filled with pure oxygen. After the system had come to equilibrium, the shaking was started and the volume of oxygen absorbed was recorded by noting the decrease of volume in the burette.

The reaction flask and capillary tubing connecting them with the burettes were filled with air. In this way a constant concentration of oxygen was maintained in the reaction flask because as the oxygen was used up in the reaction flask, it was supplied from the burette. This assumed, of course, that there is practically no diffusion of the nitrogen from the flask back through the capillary tubing, since the flow of oxygen is always toward the reaction flask and directly opposite to the direction of diffusion of nitrogen. By this method of procedure, it was found that the theoretical amount of oxygen was absorbed for complete oxidation of the stannous ions. In case a catalyst was to be added, it was placed in a capsule which could be held in the neck of the flask and dropped when desired by pulling a trigger in the side arm. The reaction was carried out at 30° unless otherwise stated.
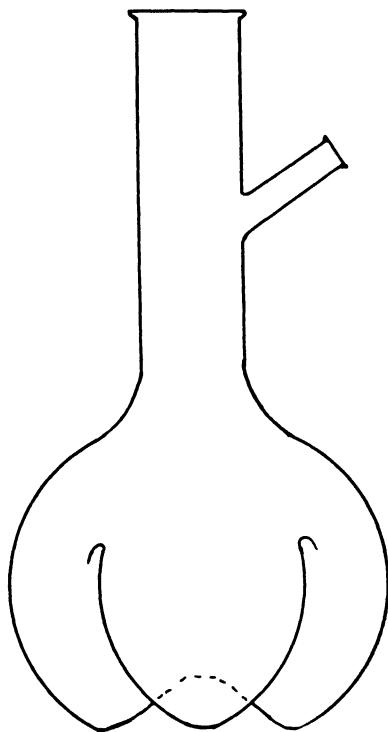
FIG. 1
Reaction Flask.

Measurement of Reaction Velocity. At the beginning the reaction showed certain irregularities so that uniform and repro-ducible results were not usually obtained until about ten per cent of the stannous chloride had been oxidized. From this period on, however, results which could be duplicated were easily obtainable. The amounts of oxygen consumed in equal time intervals were approximately equal during the first part (60%) of the experiment. In view of the fact that the solution is constantly saturated with oxygen and that the ratio of the concentration of stannous chloride to oxygen is relatively very great this would be expected. Towards the end of the run the amount of oxygen per unit time interval decreased somewhat probably due in part to decreased stannous chloride concentration and also to the using up of acid in the oxidation of the $SnCl_2$. It will be shown later that the speed of the reaction increases directly with the hydrogen ion concentration of the solu-

tion. For the comparison of experiments constants were calculated from the formula

$$K = \frac{v_0 - v}{t_0 - t}$$

in which v_0 is the volume as read on the burette at the time t_0, while v and t are corresponding values at later times. Thus K represents the average volume in cc. absorbed per minute. Table I gives the results of typical runs.

TABLE I

Data for typical duplicate runs at 30°

x = Volume of oxygen absorbed in time, t. K = x/t.

$SnCl_2$ — 14.5 g. per liter; HCl — .606 N. Gas vols. at 0° and 760 mm.

t	x	K	x	K
15	0.60	.040	0.70	.047
25	1.15	.046	1.20	.048
35	1.55	.047	1.70	.049
50	2.35	.047	2.40	.048
60	2.80	.047	2.80	.047
80	3.75	.047	3.75	.047
135	6.10	.045	6.00	.044
150	6.65	.044	6.70	.045
170	7.40	.044	7.40	.044
240	10.00	.042	10.00	.042

Factors affecting the Reaction. In order to find out whether the reaction measured was the rate of solution of the oxygen or the rate of reaction of the dissolved oxygen experiments were carried out in which the rate of shaking was increased from 900 to 1800 shakes per minute. The data in Table II indicate that for these ranges the rate of oxidation is independent of the rate of shaking and therefore it is the dissolved oxygen that is reacting. This oxygen is being supplied very rapidly, the rate of diffusion through the liquid being so rapid that there is very little difference in the concentration of the oxygen at the liquid-gas interface and the interior of the liquid. Experiment 3, Table II, shows that a non polar lining (paraffin) is without influence on the speed of the reaction. Increasing the glass surface by the addition of powdered glass (Expt. 4) is also without effect.

It was of interest to compare our method of studying this reaction with that of Miyamoto, who bubbled air into 40 cc. of $SnCl_2$ solution in a test tube (diameter 3 cm.) through a glass tube with a 4 mm. opening at a rate of 7.78 l. per hour. In our experiments air was bubbled through 125 cc. of $SnCl_2$ solution in a tube 2.8 cm. diameter, kept at 30°. The absorption of oxygen was followed by removing 5 cc. samples at definite times and titrating for the stannous tin. 9.5 liters of air per hour were bubbled through the solution through a jet with a 4 mm. opening. In another set of experiments the same

volume of air per hour was bubbled through four jets having openings between 0.5 and 0.75 mm. The concentration of stannous chloride was 36.3 g. per liter in each case with total acidity of 0.85 N HCl. With the four fine jets the speed of oxidation was about twice as great as in the case of the single larger jet. This indicates that in Miyamoto's experiments the solution was not saturated and that he was measuring two reactions—one at liquid gas interface, the other in solution.
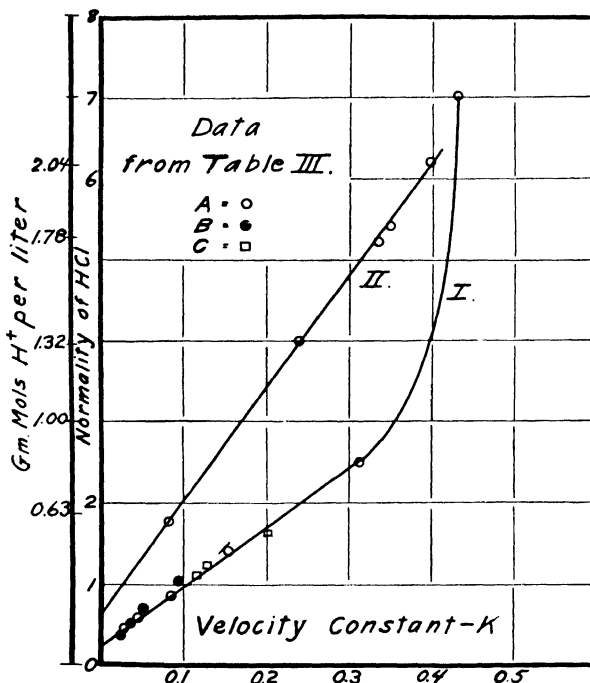
FIG. 2

Effect of HCl Concentration.

TABLE II

Expt. No.	K	Rate of shaking per minute	Remarks
1	.040	1800	Pyrex flask
2	.041	900	,, ,,
3	.040	900	Paraffin coated flask
4	.044	900	Pyrex flask + 2 g. powdered glass
Concentration of SnCl$_2$	36.3 g. per liter		Total acidity 0.85 N HCl

Effect of Acid Concentration. Within certain limits, the rate of autoxidation of stannous chloride increases with the concentration of the hydrochloric acid as shown by the data in Table III and also by Curve I, Fig. 2. While the solubility of oxygen decreases with increasing concentration of hydro-

chloric acid, the change is not great as evidenced by the solubility data of
Geffken.[4] He gives the solubility of oxygen at $25°$ as 0.0308 for water and
0.0267 for 2 N HCl. Below the concentration of 2 N HCl, then, the effect of
the solubility of oxygen is of minor importance. There is a definite upper
limit beyond which the concentration of hydrochloric acid shows little effect
on the rate of reaction. If the curve is continued downward there is a mini-
mum concentration of hydrochloric acid (0.25 N) beyond which autoxidation
would not take place. These data also show that within certain limits the
reaction is independent of the concentration of the stannous chloride (Table
III, A and C) but dependent upon the total acid concentration of the solution,
consequently the explanation of this reaction from the standpoint of a re-
action of zero order must deal primarily with the mechanism of the action of
the oxygen. It is quite possible that the oxygen functions through the
formation of a perstannate which undergoes reduction leaving the tin in the
tetravalent state. Sufficient data are not available, however, to test this
point, which will be made the subject of further experimentation.

TABLE III

The Effect of Acid Concentration on the Reaction

A		B		C	
Normality HCl	K	Normality HCl	K	Normality HCl	K
7.04	0.40	1.07	0.096	3.23	0.54
2.48	.31	.70	.054	1.63	.20
1.41	.15	.52	.035	1.22	.129
0.87	.088	.43	.027	1.09	.118
0.61	.045				
0.47	.032				

A—Contains 14.5 g. $SnCl_2$ per liter.
B—Same as A but with another sample of acid.
C—Contains 29.3 g. $SnCl_2$ per liter.

The relation of the speed of oxidation to the actual hydrogen ion concen-
tration has been calculated and graphed (Curve II) from data (Table IV)
supplied by Dr. Arthur Weber. The hydrogen ion concentrations were
measured by means of the glass electrode.

TABLE IV

Hydrogen Ion Concentration of Stannous Chloride Solutions

Concentration of $SnCl_2$ gm/l	Acidity as HCl (N)	pH	Mols of Hydrogen Ion per liter
14.65	.98	+0.20	0.631
14.65	1.96	−0.12	1.32
14.65	2.80	−0.25	1.78
14.65	4.08	−0.31	2.04
29.3	1.95	−0.05	1.12
29.3	3.91	−0.25	1.78

[4] Geffken: Z. physik. Chem., **49**, 257 (1904).

It is plain that the oxidation of stannous chloride is directly proportional to the hydrogen ion concentration between pH of $+0.2$ and -0.25.

Metallic Ions as Catalysts. Of the several salts whose effect on the reaction was tried (Table V) the outstanding example of positive catalysis was cupric chloride. With this salt the rate of reaction became a function of the rate of shaking. An increase from 900 to 1800 shakes per minute increased the constant from 1.28 to 2.49.

The action of the cupric chloride can be explained by the assumption of a reduction of the cupric to the cuprous ion by stannous chloride with a subsequent rapid oxidation of the cuprous to the cupric ion, this latter being the principal reaction. The effect of increased shaking could then be due to a catalysis of this reaction by the glass, or the rate of oxidation of the cuprous chloride might be so great that there was an appreciable drop in the oxygen concentration between the liquid surface and the interior of the liquid. To test the action of the surface of the glass, two sets of experiments were performed, one using paraffin-lined flasks and the other adding an excess of powdered pyrex glass (Table VI). Although there seems to be quite an appreciable drop in the reaction velocity in the case of the paraffined flasks there is not the expected increase in reaction velocity in the case of the powdered glass. In neither case was the reaction velocity changed enough to explain the great difference occurring with the given change in the rate of shaking. It appears as if the wax and paraffin act as inhibitors rather than that the glass acts to any great extent as a positive catalyst. It seems probable therefore that the area of the liquid gas interface exposed per minute is the controlling factor.

TABLE V

Catalytic Effect of Certain Chlorides (40 millimoles per liter)

Salt added	K	Salt added	K
$CuCl_2$	1.69	$CaCl_2$	0.79
$FeCl_3$	0.45	$CuCl_2$	1.25
$CuCl_2 + FeCl_3$	1.22	$ThCl_4$	0.049
$MnCl_2$	0.66	$NiCl_2$	0.075
$MnCl_2 + CuCl_2$	1.30	None	0.040
None	0.048		

30 g. $SnCl_2$ per liter	36.3 g. $SnCl_2$ per liter
HCl Concn. 2.1 N	HCl concn. 0.85 N

Volume of solution—15 cc.

The reaction may be expressed by the following equations:

(a) $2 CuCl_2 + SnCl_2 = 2 CuCl + SnCl_4$ (in solution)

(b) $4 CuCl + 4 HCl + O_2 = 4 CuCl_2 + 2 H_2O$ (liquid gas interface).
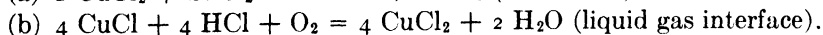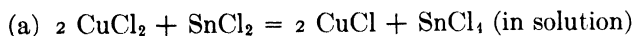
By adding cupric chloride to the solution of stannous chloride, then, the reaction becomes one of the autoxidation of the cuprous chloride instead of the stannous chloride, which autoxidation, at the rates of shaking used, becomes a reaction at the liquid gas interface.

TABLE VI

Factors influencing the Cu^{++} catalysis of the autoxidation of $SnCl_2$[1]

30 millimoles of $CuCl_2$ per liter

	Shakes/min	K
Glass capsule, glass flasks	1800	2.49
Wax capsule,[2] glass flask	1800	1.83
,, ,, ,, ,,	900	.98
,, ,, paraffined ,,	900	.73
Glass capsule and flask $\big\}$ + 2 gms. of powdered glass	900	1.60
Glass capsule and flask $\big\}$ + 1 gm. of powdered glass	900	1.53
Glass capsule and flask	900	1.3

[1] Conc'n of $SnCl_2$ 36.3 g/l. Total acidity 0.85 N HCl. 15 cc. sample.
[2] The capsules were used to add $CuCl_2$ to the $SnCl_2$ solution. Those of wax were made of equal parts of beeswax and paraffin.

Temperature Coefficient. By changing the reaction temperatures from 30° to 40°, the velocity constant for the autoxidation of $SnCl_2$ changed from 0.041 to 0.085. This is again in disagreement with the findings of Miyamoto who reported only a very slight change in the rate of reaction with a change of 10°. This difference may be explained by the fact that Miyamoto was not working with a reaction in solution. The change in reaction temperature of ten degrees would not cause a great change in the rate at which oxygen diffuses across the liquid gas interface. While the temperature coefficient is affected by the solubility of oxygen, this effect would be a decrease of about 15 per cent only, consequently the temperature coefficient would be still higher if the concentration of oxygen was the same for the two temperatures.

The Autoxidation of Cuprous Chloride

The catalysis of the autoxidation of $SnCl_2$ shown by $CuCl_2$ led to a study of the autoxidation of CuCl solutions. Below a rate of 1800 shakes per minute, the rate of shaking determines the rate of autoxidation of the cuprous ions. (Table VII.) It was impractical to attempt a rate greater than 1800 shakes per minute, because even at this rate the reaction flasks were often broken. The data in Table VII indicate that, under the conditions of these experiments, saturation was not being maintained and that the reaction was taking place mainly at the liquid gas interface. As a consequence these experiments are largely empirical, necessitating a constant rate of agitation. It was found that reproducible results could be obtained with 900 shakes per minute. Experiment 3, Table VII, in which powdered glass was added and 4, in which a paraffin-lined flask was used, show that the glass surface of the flask is practically without effect in this reaction. Experiments 5 and 6 show the effect of the degree of dispersion of air bubbles on the autoxidation of CuCl by bubbling air through the solution.

TABLE VII

Physical Factors affecting the Rate of Autoxidation of Cuprous Chloride
(2.1 N HCl) CuCl– 15 g. per liter

No.	Volume of Solution	Rate of Shaking	K	Remarks
1	15 cc.	1800	3.25	
2	20 cc.	900	1.24	
3	25 cc.	900	1.32	1 gram of powdered glass
4	25 cc.	900	0.94	Paraffin lined flask
*5	95 cc.	—	0.087	Three jets, 0.5 to 0.75 mm. bore
*6	95 cc.	—	0.052	One jet, 4 mm. bore

* 10 liters of air per hour bubbled through 95 cc. of solution, 17 cm. deep. The reaction was followed by adding a sample of cuprous chloride to an excess of potassium dichromate and titrating the excess with standard titanous sulfate.

The Effect of Salts on the Rate of Autoxidation of Cuprous Chloride. In every case the addition of a salt diminished the rate of reaction, even in the case of added cupric chloride. Using 25 cc. of solutions of cuprous chloride of acid concentration 2.1 N, the following values of K were obtained with the following salts; 30 millimoles per liter of each salt being used: Co^{++} 1.18; Ni^{++} 1.10; V^{++++} 1.03; U^{+++} 0.95; Th^{++++} 1.15; Mn^{++} 0.97; Fe^{+++} 1.26; CuCl alone 1.28. This does not mean that some of these salts would not act as positive catalysts provided the reaction observed was one in solution rather than one taking place at the liquid gas interface. In a reaction of the type at hand, an increase in the rate of reaction when the oxygen was being used up at a greater rate than the rate at which it was being supplied through the liquid gas interface would be improbable. No doubt the decrease in the rate of reaction in the presence of these salts was due to the formation of complex ions which are not oxidized by the dissolved oxygen or, at least, are oxidized at a much slower rate than the cuprous chloride.

Similar results were obtained by the addition of sodium chloride to the cuprous chloride solution in the following amounts: 0.5 g, 1 g, 2 g, which gave values of K as follows: 1.25, 1.10, 0.93, while 1 g of $CuCl_2$ gave a value of 1.10. K for cuprous chloride alone was 1.38.

A change from 30° to 40° had very little effect on the rate of reaction, which is characteristic of a surface reaction of this type. The acid concentration had very little effect upon the rate of reaction, the value of K for normality 3.45 being 0.87 while for 5.73 N HCl the value was 0.84. Whatever effect was observed indicates that the reaction tends to decrease in speed with increase in acid concentration, which may also be due to the complex ion formed in solution.

Induced Reactions. The oxidation of cuprous chloride in the presence of the following compounds: arsenious acid, phosphorous acid, hydrazine sulfate, citric acid, and tartaric acid was tried. It was found that the oxidation of

cuprous chloride caused a slight oxidation of all the materials tried with the exception of hydrazine sulfate which was not oxidized and phosphorous acid which autoxidizes in the presence of sufficient hydrochloric acid and cupric salt.

The effect of the concentration of the salts used in these experiments upon the solubility of oxygen has not been discussed. From consideration of the work of MacArthur[5] it seems, however, that as the concentration of the salt increases the solubility of the oxygen decreases. It follows then that the change in concentration of the stannous chloride in Table IV would cause some change in concentration of the dissolved oxygen, but this change in concentration was negligible.

The autoxidation of stannous chloride is believed to be unusual in that the rate of autoxidation increases with the increase of acid concentration while the general tendency is for compounds to become more stable towards oxygen with increasing acid concentration.[6] The increase in reactivity with higher concentrations of acid may be due to catalysis by hydrogen ions, in much the same way as many other reactions are catalyzed by hydrogen ions. It has been shown that the rate of reaction is in direct proportion to the hydrogen ion concentration. It is also possible that at the higher concentrations of acid the formation of salt solvent complexes may play a part. There is also the possibility that the oxidation of the Sn^{++} ion occurs at a different rate than the SnO_2^{--} ion, which would also account in some measure for the effect of the hydrogen ion concentration of the solution. The whole problem is complicated by the extent of hydrolysis of the tin salts, a subject which is now under investigation.

These experiments with stannous and cuprous chlorides illustrate two extreme possibilities of autoxidation. The one is the case in which the oxygen is being supplied at a rate greater than the rate of autoxidation in which case the dissolved oxygen comes to equilibrium with the gaseous oxygen at the partial pressure in the gaseous phase. In the other case, the autoxidation is more rapid than the supply of oxygen and the reaction takes place at the liquid gas interface while the interior of the liquid may be almost void of dissolved oxygen.

Summary

1. The autoxidation of stannous chloride occurs in solution as is evidenced by the high temperature coefficient and the fact that an increase in the liquid gas interface does not cause an increase in the rate of autoxidation.

2. Within certain limits the rate of autoxidation of stannous chloride increases directly with the increase in the acid concentration, and is directly proportional to the hydrogen ion concentration.

3. Within certain limits the rate of autoxidation of cuprous chloride is independent of the acid concentration.

[5] MacArthur: J. Phys. Chem., **20**, 495 (1916).
[6] See Lamb and Elder: J. Am. Chem. Soc., **53**, 147 (1931).

4.   The catalytic effect of a number of salts on the rate of autoxidation of stannous chloride has been investigated.   Cupric chloride was outstanding in its catalytic activity, which is explained by a cycle of oxidation and reduction involving the cupric and stannous chlorides and dissolved oxygen.

5.   Of the investigated salts, none was found to increase the rate of autoxidation of cuprous chloride.

6.   The autoxidation of the cuprous chloride induced the oxidation of citric and tartaric acids as well as of arsenious acid.

7.   Certain published results on the autoxidation of stannous chloride which differ from the data obtained by the authors are apparently due to experiments with unsaturated solutions of oxygen.

Madison, Wisconsin.

THE PHOTOCHEMICAL INTERACTION
OF ACETYLENE AND WATER*

BY ROBERT LIVINGSTON AND C. H. SCHIFLETT

It has been reported by Reinike[1] that the photochemical polymerization[2] of acetylene is disturbed by water with the resultant formation of an aldehyde. The work presented here was begun in an attempt to isolate the products of this reaction between acetylene and water.

The Reaction in the Gas Phase[a]

To minimize the photolysis of any possible products of the reaction, a flow system was used. Acetylene was taken from a commercial tank (acetone solution) and was passed through a series of wash bottles, which contained the following reagents in the order named: sodium bisulfite solution, concentrated sulphuric acid saturated with potassium dichromate, concentrated sodium hydroxide solution, and distilled water. After leaving the wash bottles, the gas passed through a plug of glass wool, and then downward through a quartz tube, of 4 mm. inside diameter and 12 cm. length, which was bent into a zigzag and was joined to the glass apparatus by silver chloride seals. A trap was sealed just below the quart zigzag, and was followed by a second trap which was kept at about 1°C by means of a water bath. Before leaving the apparatus, the gas passed through a wash bottle containing distilled water. The light source, a vertical Cooper-Hewitt quartz mercury arc, operating at from 3.5 to 4.0 amperes, was placed about six centimeters in front of the quartz zigzag.

After each run the traps were washed with conductivity water. The washings of the traps and the distilled water from the final wash bottle were tested for acids and aldehydes. Methyl red was used in the test for acid and Schiff's reagent (magenta decolorized with sulphur dioxide) in the test for aldehyde. Several experiments were performed over periods which ranged from twenty minutes to two and a half hours. In no case (when pure acetylene was used) was there a positive test for either acid or aldehyde. In contrast to this result, if a mixture of oxygen and acetylene was irradiated under the same conditions, a trace of aldehyde and quantities of oxalic acid up to 6×10^{-5} equivalents were found.[3]

The Reaction in Aqueous Solution

In a second attempt to determine if there is any reaction between acetylene and water, a saturated aqueous solution was irradiated.

The method of purification of the acetylene has already been described. The reaction vessel, a thin-walled quartz cylinder, is represented in Fig. 1. The ends of the cylinder (A) were ground into pyrex caps and sealed with silver chloride. A slow constant current of acetylene was injected into the side tube (C) at (D), and served the double purpose of keeping the solution saturated and stirred. The excess gas escaped through the water trap (E). In many of the experiments the solution was kept cold by flowing ice water first through a glass coil immersed in the reaction vessel and then through a jacket surrounding the side tube. The light source which was a vertical quartz mercury arc operating at 30 volts and 4.0 amperes, was placed approximately one inch from the reaction vessel.
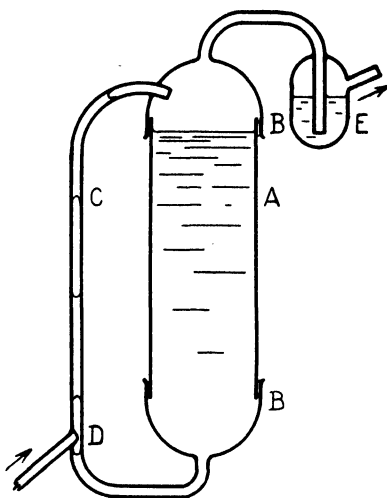
The duration of the individual experiments varied from ten minutes to four hours. After each experiment the solution was removed and tested for reaction products. In no case did the solution give a positive test for acids, aldehydes, ketones, or alcohols.[4] The only product was an inert whitish substance, which formed chiefly on the wall of the cylinder nearest the light source. This substance formed to some extent throughout the solution, giving it an opalescent appearance. It is insoluble in ordinary solvents, and, although it differs somewhat in appearance from cuprene, it is very probably a polymer of acetylene.

Fig. 1
Reaction Vessel.

Summary

Neither gaseous acetylene saturated with water vapor nor an aqueous solution of acetylene formed detectable quantities of aldehydes or acids when exposed (in the absence of oxygen) to the complete radiation of a quartz mercury arc.

Minneapolis, Minnesota.

[1] The analytical methods described in Kamm's Qualitative Organic Chemistry were used.

THE CO-ORDINATION OF PERIODIC STRUCTURES

BY MAURICE COPISAROW

In this paper experiments are described, which may serve as a link between isolated physical and chemical cases of periodicity—thus co-ordinating a range of periodic structures on the basis of a gradation in complexity. Such co-ordination or continuity is essential in any attempt to postulate a general principle of periodicity.

Commencing with the physical or simpler aspect of the problem we find periodic structures to be formed by finely divided solids under the influence of a vibrating column of air[1] or steam.[2,*]

Periodic formations observed on surfaces of liquids, viz:—concentric rings, etc., belong to the same category but are more temporary in character.

To this range of physical rhythmic forms we have also to add formations produced by condensation or change of phase.

The huge movement of water vapour in the atmosphere produces under favourable conditions a stratified suspension of water particles in clouds.

In the course of the present investigation a striking example of such periodic structures produced by condensation—the transformation of carbon dioxide gas to its solid phase—was observed.

A current of carbon dioxide gas from a cylinder was allowed to pass through a horizontally placed open glass tube, five feet long and one inch in diameter. The tube was wrapped in cotton wool and cooled with ether, the pressure of the gas remaining constant throughout the experiment. This was ensured by employing practically full cylinders for each experiment and observing the constancy of the sound note emitted by the tube.[**]

After an exposure to the current for ten minutes, the walls of the tube were found to be uniformly frosted. Reporting the experiment with an increased pressure of the carbon dioxide current (uniformity of sound being maintained) thickish bands of $1\frac{1}{2}$-2 inches in width were found to be alternated by cloudy regions of similar size. The range of these bands extended for a distance of approximately 22 inches.

Carrying out a series of experiments, gradually increasing the pressure of the gas, but keeping it constant for each separate case, the snow drifts representing the thick bands became narrower and more sharply defined, becoming ultimately thick ridges or even perforated discs, a $\frac{1}{4}$-$\frac{1}{3}$ inch in thickness separated by cloudy regions of 1-$1\frac{1}{2}$ inches.

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* Even here the problem is not free from complexity. The dust ridges appear as the outcome of the combined influence of turbulent or general circulation and vortex motion (Andrade: Nature, **1931**, 438; Patterson and Cawood: 667).

**The use of a manometer or wind gauge was found unsatisfactory, owing to the interference of carbon dioxide snow. This snow-choking was found occasionally to obstruct the maintenance of a regular current. The reflection waves produced by the vibration of the glass walls, were another source of disturbance which was only partially overcome by efficient clamping and embedding in cement of both ends of the tube.

Whilst no exact temperature can be stated to correspond to each particular experiment, in general the band formation became more defined with the fall of the temperature—the wide bands appearing at approximately $-45°$ reaching their sharpest form at $-78°$.

An interesting, somewhat parallel case of banded formation is that of volatilization and condensation of ammonium carbonate. Finely powdered ammonium carbonate (15–20 grs.) was put in the sealed end of a horizontally placed 60 × 1 inch glass tube. Heating the end of the tube containing the salt over a spirit lamp, the salt volatilized, the tube assuming a uniform cloudy appearance for a distance of about 20 inches.
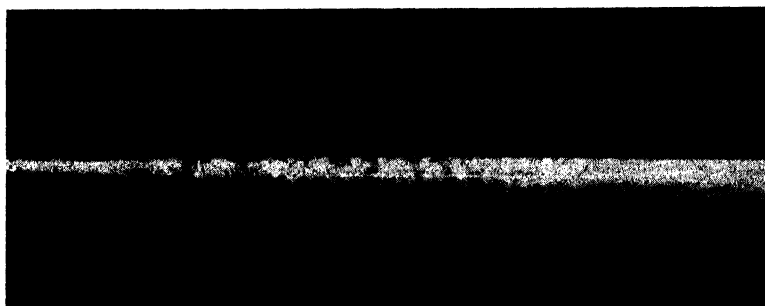
FIG. 1

Volatilizing at a much higher temperature by placing the sealed end in a 2 KW electric heater the following results were obtained. The reaction seemed to proceed in stages with rise of temperature. A liquid magma was found to be deposited along the bottom of the tube in the section adjacent to the heated end, the cloudy frostiness drifting gradually further away. As the temperature rose still higher, large well-developed crystals in a variety of pretty patterns appeared in the clear portion of the tube nearest to the heater. Simultaneously with this the viscous mass covering the bottom of the tube for a distance of about 15 inches underwent a change, becoming rugged with a jagged outline. The mass gradually split up into a series of parallel ridge formations, wide in the centre, tapering at both ends (Fig. 1). The ridges reminiscent of Kundt's figures, extended over a distance of 12–15 inches, the spacing between the tapered ends of adjacent ridges gradually increasing from 2/5 to 3/5 of an inch.

Allowing the tube to stand for about a week at 18°, part of the ammonium carbonate evaporated, the appearance of the ridge formations undergoing a change, assuming a sharper outline. The tapering and sloping ends gradually faded away, the central elevated portion becoming a range of sharply defined barriers (Fig. 2).

An attempt was made to regulate the different stages of reaction described above. It was found during the heating of the ammonium carbonate that sound could be distinctly heard at the open end of the tube. Commencing with a crackling noise of a varying note, the sound gradually rose to a definite

pitch very akin to the pulsating sound of a distant dynamo. With the exhaustion of the ammonium carbonate in the tube the sound lost its regularity, resolving itself into crackling and spluttering.

From a number of experiments it was found that the liquid and cloudy deposits were formed during the period preceding the rise of temperature associated with a regular sound wave. The range of reaction involving the symmetrical ridge formation lay within the region of constant pitch, whilst the large crystal clustering was produced during the last stage of heating. The following experiment illustrating these features gave satisfactory results.
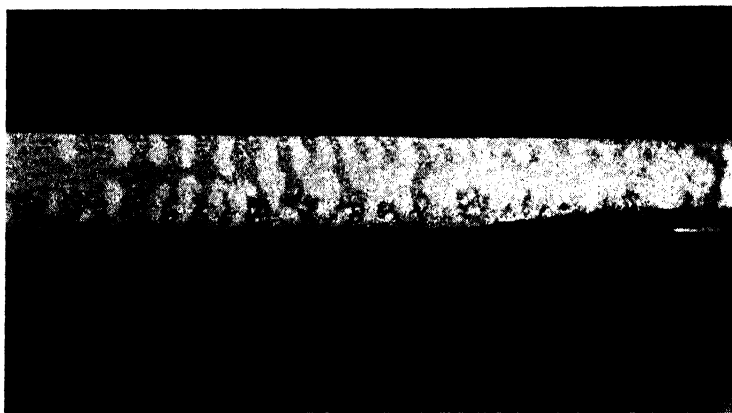
Fig. 2

Powdered ammonium carbonate was heated in a 6 × 1 inch test tube, connected by means of a tight fitting vulcanised rubber band to a 60 × 1 inch glass tube. The latter was replaced from time to time by others of equal size, their replacement being regulated by observation of the depositions as well as by the sound. In this manner separate tubes were obtained, the deposits in which represented the various stages of volatilization. Even here a perfect subdivision of the reaction stages was impossible owing to the fluctuation in temperature during the transfer of tubes.

Using a ½ inch bore tube the general features of the volatilization were in the main the same. The ridge formation was finer in outline, extending over 5 to 6 inches with about eight to ten parallels to the inch.

Replacing ammonium carbonate by ammonium carbamate, the striations and the whole character of the condensation were found to be essentially similar.

The deposition was however less compact, the structures consisting of clusters of macroscopic needles.

The distillation of urea under similar conditions was accompanied by considerable decomposition. The indication of rhythmic band formation was slight but definite.

These experiments (carbon dioxide and ammonium carbonate) show that the magnitude of both energy changes, and general experimental conditions varies greatly with each particular case.

Extending our investigation to cases in which chemical reaction makes an appearance, we find that whilst additional complexity is introduced, the fundamentals outlined previously still hold good.

Thus the introduction of such new influences as chemical affinity, frequent appearance of a new component in the system in the form of the product of reaction, etc., does not alter the basis or crucial points of rhythmic movement and its material record.

In the case of the ignition of explosive mixtures of gases the oscillatory vibrations produced by the detonation wave are very much akin, if not identical to the vibration columns produced by sound waves.

This is supported by the striation of luminous dust particles in the trial of the explosion wave[3] as well as by periodic structures produced either by the product of reaction[4] or by originally present finely divided matter.[5]

The combination of magnesium metal with oxygen affords an example of a periodic structure as a result of combustion.

For this experiment a horizontally placed glass tube, 60 inches long, ½ inch in diameter was employed. A small bundle of magnesium ribbon was inserted in the front end of the tube, the glass being protected by an asbestos cylinder surrounding the magnesium. Igniting the magnesium ribbon the dense white fumes partly escaped through the front opening and partly were deposited along half of the length of the tube. On examination a succession of opaque and opalescent bands (1.5 inch wide) were found to be formed. The bands appeared to decrease in density with the distance from the front end of the tube, and opaque bands gradually becoming opalescent areas divided by clear spaces. Using one inch bore tube with a correspondingly increased quantity of magnesium ribbon an essentially similar effect was obtained. However, the bands were wider and vanished within 20 inches.

In several instances the combustion of the magnesium ribbon inside the tube was found to be sluggish; the white fumes slowly advancing in a spiral manner along the tube were ultimately deposited as a uniform layer. This slow combustion could be avoided by the introduction of oxygen or oxygen yielding substances such as potassium chlorate or perchlorate.

Interesting results were obtained in vertically placed tubes. The magnesium, supported by copper wire, was lighted in the asbestos lined upper portion of the tube. The rhythmic effect became somewhat blurred, the opaque bands, although occurring at regular intervals, becoming incomplete. It was noted that the opaque portions of the bands, occupying between a ¼ and ½ of the cross section of the tube were not in the same plane. The opaque patches were found to be in approximately the following order: front of tube, left side, back, right side, front again and so on—showing the course of the fume passage to be spiral. This screw-like path was graphically shown by omitting the copper wire. The expanded magnesium ribbon held by the

asbestos, was set on fire, and with a roar swiftly dropped down the tube as a ball of dazzling white flame. Examining the tube it was found that the spirally placed incomplete bands were enhanced in opacity, these bands being joined by an opaque spiral line, about a $\frac{1}{4}$ inch in width.

The thickness and number of turnings of the spiral were observed to be related to the quantity or rather volume of the magnesium ribbon employed. Increasing the quantity of the metal the number of turnings was reduced whilst the spiral became more distinct.

Allowing small pieces of ignited magnesium ribbon to drop down the tube it was observed that whilst the course of the burning wire was practically vertical, it was followed by a white spiral trail of about $1\frac{1}{2}$ to 2 inches in length, the number of turnings being about 4-5 to the inch.

The phenomenon vanished rapidly, leaving in this case no outline of the spiral movement on the walls of the tube.

Replacing magnesium by yellow phosphorus in horizontally placed tubes no rhythmic deposition could be observed. Owing to the protracted combustion the clearly visible spiral or wavy movement of the vapour was found to result in a succession of overlapping layers.

Here we have to refer to an interesting spiral movement of condensing vapour, observed in the cases of the ammonium salts and phosphorus. Viewing the open end of the tubes during the period of uniform condensation as indicated by the constancy of sound, the vapour, invisible in the upper part of the tube, was found to drift slowly in two distinct separate spirals along the lower half of the tube. The spirals, which were of a whitish fog consistency, seemed to be almost stationary in their outline and directed—the right spiral clockwise and the left counterclockwise. The regularity of the spirals was readily disturbed by a change in the air current at the open end of the tube, the whole cross-section becoming filled with whitish vapour.

It would seem to the author that this phenomenon may be accounted for by the fact that originally the condensation of the vapour commences simultaneously on both sides of the tube, the upper hotter part of which remains clear; a portion of this condensation product is so finely divided as to persist as a fog, which advancing along the lower part of both sides of the tube forms two separate spiral currents. This appears to be fairly general to slow condensations, as a similar effect was noted in the distillation of salicylic acid and phthalic anhydride.*

Owing to the great dispersion of the fog spirals they could be discerned only when viewed edgewise in the direction of the long axis. The accompanying graphic representation of the phenomenon, though exaggerated, gives a fair idea of the actual more nebulous helices (Figs. 3 and 4).

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* Here we have sections of a system function in a manner independent from one another —a feature frequently met with in the formation of periodic structures. In nature we find many parallels to this. In oceanography and still more meteorology—currents, vortices, spouts, cyclones, and anticyclones—are all examples of such a phenomenon on a gigantic scale.

The experiments described above show clearly that a definite uniform frequency rather than velocity of reaction is essential in rhythmic formations. We may reduce detonation and combustion to slow diffusion without impairing the possibility of striations, provided such wave-frequency and adequate amplitude are maintained; in other words, so long as there exists a suitable relationship between the vibration column and the boundaries of the system.

Some systems, owing to their inherent slowness of reaction, can acquire a wave frequency and amplitude adequate for band formation only by a special reduction in their boundaries. All other conditions being equal—frequency increases with the diminution of the vibration system.

In cases where the components, initially gaseous, are transformed to the liquid or solid phase, we are gradually driven to confine ourselves to restricted systems such as tube experiments. These tubes narrow down as our components lose their gaseous character, until ultimately we arrive at two-liquid component systems, in which case adequate wave frequency and amplitude are confined to *capillary* tube experiments.
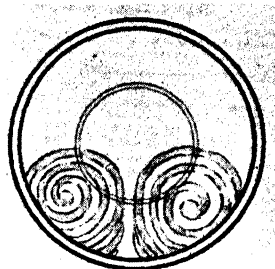
FIG. 3
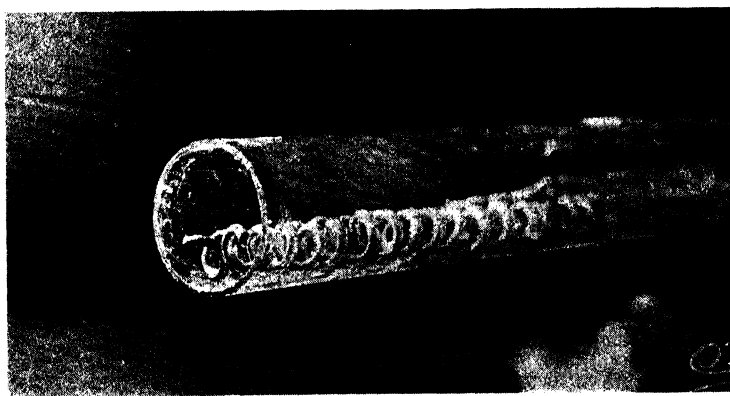
FIG. 4

Now let us consider a few cases of rhythmic formation, in which comparatively slow chemical reaction is the motive force. König[6] and Hedges[7] obtained rhythmic bands of ammonium chloride by allowing hydrogen chloride and ammonium gas to diffuse into a tube from opposite directions. Likewise a banded deposition of sulphur was produced by the interaction of hydrogen sulphide and chlorine.[6]

In the present investigation rhythmic structures of ammonium carbamate were obtained in a similar manner.

Passing a slow current of dry ammonium gas and carbon dioxide simultaneously from both ends of a 60 × ¼ inch tube, a series of perforated discs

separated by cloudy regions were obtained (12 discs spread over an area of 18 inches).

Allowing carbon dioxide to diffuse slowly into a 60 × 1 inch tube filled with ammonium gas, the periodic structures spread over a range of 20 inches took the form of white short and hairy fibres clustered together into patterns resembling fir trees. The growth extended over about $\frac{1}{3}$ of the cross section of the tube at intervals of 1.5 to 1.75 inches.

An interesting periodic effect was observed in a horizontally placed 60 × 1 inch tube, the bottom of which was covered with concentrated ammonia. The thick masses of ammonium carbonate formed in the upper part and sides of the tube assumed a curved striated form. Owing to the sliding and folding of the ammonium carbonate its general aspect was that of glaciation.

As we pass from the gaseous mixtures to the liquid component systems the process of diffusion becomes so slow, that the whole system may be regarded as consisting of a number of sections or a series of apertures. Thus the length of the system ceases to be one of the decisive factors, the problem being dominated by the relationship of the wave-frequency and amplitude to the orifice or diameter of the system. For this reason the capillary tube experiments may be carried out with equal success either in tubes,[8,9] or between microscopic slide-covers[10] or in finely powdered materials such as gypsum, ground glass, sand, etc.[8,11]

These capillaries represent the limit to which external boundaries may be reduced. Beyond this they lose their significance, their place being taken by the inner structure of the system.

The smallness of boundaries and fineness of division or in other words the large surfaces attained by minute orifices in capillary tubes and finely divided matter ultimately lead us to a critical point, at which the aggregation of particles becomes practically molecular, as is the case with colloids.

In the case of colloids their complexity makes them more susceptible to functional influences, with the result that we are faced with a remarkable variety of rhythmic forms.

The extreme difference in conditions and appearance of the physico-chemical complexes underlying these periodic structures may be seen in many natural formations, Liesegang, stratified, refraction and opacity bands as well as spiral, meshwork and cellular structures including arboreal or mineral-tree growth.[12]

Conclusion

The experiments described in this paper represent a connecting link between hitherto disconnected periodic phenomena. The co-ordination so introduced makes one general feature stand out clearly, namely, that periodicity is dominated by transition, movement or change of phase rather than by any specific condition or number of components.

Bibliography

[1] Kundt: Pogg. Ann., **127**, 497 (1866); Carrière: J. phys., **1929**, 198; Irons: Phil. Mag., **7**, 523 (1929); Andrade and Lewer: Nature, **124**, 725 (1929).

[2] Crews and Hymas: Nature, **124**, 793 (1929).

[3] Dixon: Phil. Trans., **200 A**, 326 (1903).

[4] West: Nature, **113**, 712 (1924).

[5] Campbell and Finch: J. Chem. Soc., **1928**, 2094.

[6] König: J. Phys. Chem., **24**, 466 (1920).

[7] Hedges: J. Chem. Soc., **1929**, 1848.

[8] Ostwald: Kolloid-Z., **40**, 144 (1926).

[9] Hedges: J. Chem. Soc., **1929**, 2779.

[10] Notboom: Kolloid-Z., **32**, 247 (1923).

[11] Liesegang: Wiss. Forschungsber., **4**, 80 (1922).

[12] Copisarow: J. Chem. Soc., **1927**, 222; Kolloid-Z., **44**, 319 (1928); **49**, 309 (1929); **47**, 60 (1929); Emich: Monatshefte, **50**, 269 (1928); Bary: Rev. gén. Colloïdes, **6**, 209 (1928); Bary and Rubio: **7**, 308 (1929); Keenan: Kolloid-Z., **47**, 289 (1929); Schultze: **50**, 106 (1930); **51**, 289 (1930).

Research Laboratory,
145 Alexander Road,
Manchester.
October 14, 1931.

NEW BOOKS

Nucleic Acids. *By P. A. Levene and L. W. Bass. 23 × 15 cm; pp. 337. New York: Chemical Catalog Company, 1931. Price: $4.50.* This is one of the American Society Monographs. In the preface the authors say: "The chemistry of nucleic acids can be summed up very briefly. Indeed, a few graphic formulas which need not fill even a single printed page might suffice to express the entire store of our present-day knowledge on the subject. Yet a detailed formula expressing the arrangements of all the atoms entering in the structure of the molecule of nucleic acids is the result of the combined labors of many chemists, the list of whom is headed by Scheele, who was born in 1742 and died in 1786. Somehow, every point in the structure of nucleic acids was reached with great difficulty by the paths of error and controversy. Theories had been advanced and had been abandoned but even the errors often led to true progress and it would be an injustice to many if the monograph contained only the views that seem correct today. Hence, the historical method of discussion was adopted in this monograph. It was hoped that this method would lead to an unbiased presentation of the material; yet we fear that unintentionally some contributions may have been overlooked", p. 7.

The book is divided into two parts, entitled Components of the Nucleic Acids and The Nucleic Acids. In Part I the chapters are: sugars, imines, imido esters, and imidazols; pyrimidines; uric acid and purine; purine bases; nucleosides; and nucleotides. In Part II the chapters are: the discovery of nucleic acids and of their components; structure of nucleic acids; nucleic acids of higher order; nucleases.

"Imperfect as is the present-day knowledge of the chemistry of nucleic acids, yet it is able to disclose much of the mystery of their biological synthesis and of their degradation. In its simplest form nucleic acid is an ester of phosphoric acid and an organic radicle, the latter consisting of a sugar and a nitrogenous component which is a cyclic derivative of urea. The moment chemistry has succeeded in formulating nucleic acid in these terms, it has indicated the way of its formation from carbonic acid, ammonia, and phosphoric acid. It has long been known that the plant is capable of reducing carbonic acid to formaldehyde and of condensing this into sugar. It is also long known that urea can be derived from carbonic acid and ammonia; in fact, urea is a partially ammonized carbonic acid. As an aquoammono derivative of an organic acid, urea represents a particular substance of a large group of analogous substances widely distributed in animal and plant tissues.

"The one peculiarity that is common to all substances of this group is the readiness with which they suffer intramolecular rearrangements under the influence of external conditions. Every rearrangement naturally leads to an alteration in the chemical functions of the substance. In the living organism every change in chemical function may and perhaps always does lead to a change in biological function. If for a moment one stops to think that nearly every biologically important organic molecule contains at least one and most frequently many such dynamic groups, and that the number of them in a single cell is beyond count, he will realize what a sensitive instrument the cell is. If he will further bear in mind that most of the changes here referred to are reversible, and that even in a simple solution of a single substance the ratio between the two forms can be discovered only with great difficulty, he will realize the obstacles that the biologist must encounter on his way when he attempts to correlate biological function with chemical change," p. 12.

On p. 41 the authors give graphic formulas for the enol and the keto form of uracil; but they do not point out that the enol form would add one hydrogen chloride stoichiometrically and the keto form none. Since uracil does add one hydrogen chloride stoichiometrically the solid cannot be the keto form. This does not necessarily have the enol form as written because there are other possibilities not discussed by Levene and Bass. On p. 63 they say that uracil does not combine with acids.

"The free base [cytosine] crystallizes out in bright platelets with mother-of-pearl luster,"

"The observations of Brugnatelli and of Prout are the last made in the period of the primitive phase of organic chemistry. They have a more or less casual character. By itself, the discovery of a new substance was in those days a great event, and to establish connection between the newly discovered compound and the parent substance was beyond the power of chemistry at that time. The search for new substances rather than the finding of relationships was the dominant incentive even in the following period when the chemist was already in possession of quantitative analytical methods. This peculiarity comes to light very strikingly when one reads side by side the classical contributions of Wöhler and Liebig and of Baeyer. It will be seen later that Baeyer in a way may be regarded as the interpreter of the findings of Wöhler and Liebig, a relationship which in no way detracts from the importance or from the value of Baeyer's contributions," p. 78.

"The workers who were principal figures in the development of uric acid chemistry, namely, Liebig and Wöhler and Baeyer, were inclined to derive the substance from aminobarbituric acid. It is possible that the formulation of Medicus was inspired by what may be termed the instinctive feeling of the great chemist. The graphic formulas of Medicus and of Fittig, however, were no more than probabilities, no more than hypotheses, and were not theories rigorously," p. 88.

"One might have said that the syntheses of uric acid by Behrend and Roosen and by Fischer established the structure of uric acid sufficiently well to make additional evidence in favor of the Medicus formula superfluous. In recent years, however, there have come to light many instances of migration of groups in course of a synthesis, and therefore any theory of structures established on synthesis alone gains in value when it is substantiated by some other independent methods.

"Thus, to sum up, the contributions of Fischer to the theory of the structure of uric acid are the following: He accomplished a synthesis of uric acid by a method that indicates a union of the second urea rest to carbon atoms (4) and (5) of the pyrimidine nucleus. He synthesized all the mono-, di-, and trimethyl derivatives that are postulated by the theory of structure expressed by the formula of Medicus. He demonstrated the presence of a double bond between carbon atoms (4) and (5) as required by this theory. He converted uric acid into trichloropurine, which is theoretically possible only when uric acid has the structure assigned to it by the same theory. And, finally, he converted uric acid into purine, the nucleus of all naturally occurring substances related to uric acid," p. 93.

"The significance of the nucleosides in the development of the theory of the structure of nucleic acids was manifold. Their discovery at once ended the dispute as to whether the bases in the molecule of nucleic acid are attached to the sugar or to the phosphoric acid. They furnished a rational explanation of many physical and chemical properties of the simple and complex nucleic acids. One of the most important practical interests of these substances lies in the fact that through them it was possible to isolate the sugars of the nucleic acids in crystalline form and thus to reveal the structure of these peculiar sugars. Thus far they have not been found in any other combination save in connection with nucleic acids.

"The name 'nucleosides' was assigned to the substances of this group for the reason that, on one hand, they contain sugar in a glucosidic union, and, on the other, the substances linked to the sugars are nuclein bases. It is evident that the physical and chemical properties of each individual nucleoside are the resultants of the individual peculiarities of the sugar and of those of the base. In the discussion of their properties, nucleosides may be classified, therefore, according to either the sugar or the base. It may be expedient, however, to classify them first according to their sugar and then subdivide each group according to the base. The principal reason for this preference lies in the fact that each of the complex nucleic acids contains only one sugar and four bases, and, furthermore, for the reason that ribose characterizes the plant nucleic acid and desoxyribose the thymonucleic acid. Thus, in a way, the sugar always reveals the origin of the nucleoside; the base in some cases only.

"Thus far there have been discovered in nature four different sugars linked in glucosidic union to nuclein bases, namely, ribose, desoxypentose, methylthiopentose, and glucose.

Each of the latter two sugars has been found in a single nucleoside. The following four types will be discussed, and when necessary, they will be subdivided according to the type of the base.

    1. Ribosides.
          a. Purine ribosides.
          b. Pyrimidine ribosides.
    2. Ribodesosides.
          a. Purine ribodesosides.
          b. Pyrimidine ribodesosides.
    3. Adenine methylthiopentoside.
    4. Pyrimidine hexoside (glucoside).

"This classification refers to the naturally occurring nucleosides only. Synthetic nucleosides have been prepared from several common sugars, namely, from derivatives of glucose, galactose, rhamnose, arabinose, xylose, and ribose. All these synthetic nucleosides will be discussed in the section on ribosides according to the component base. The reason for this arrangement lies in the fact that the details of the structure of nucleosides were worked out on the ribosides, which are by far the most accessible and which chronologically were the first to be obtained from nucleic acids," p. 126.

"In justice to Haiser and Wenzel it must be said that their conclusion was partly due to the fact that they had relied upon the data of Neuberg on the properties of the phenylosazone of the sugar obtained from inosine. Later they took the mixed melting-point of the two benzylphenylhydrazones, namely, of lyxose and of the sugar from inosinic acid. The individual hydrazones had nearly identical melting-points, that of lyxose melting at $127\,°$C. and the other at $129\,°$C. The mixed melting-point, however, was $40\,°$ below the values of the individual compounds. Furthermore, they found that the p-bromophenylhydrazone of the sugar from inosinic acid has the same properties as van Ekenstein and Blanksma described for ribose. The authors then accepted the conclusion of Levene and Jacobs on the ribose configuration of the sugar," p. 134.

"This gelatinization of guanylic acid requires special discussion. It is not caused by the colloidal nature of the acid, but is due to the presence in its molecule of guanosine, which, in the presence of impurities, settles out of aqueous solution in gel form. This peculiarity was observed by Levene and Jacobs in their early work on guanylic acid. It was then stated that the product of neutral hydrolysis of nucleic acid on cooling turned into a semi-solid gel. Very minute quantities of mineral impurities suffice to bring about gelatinization. In excess of alkali, this gel is soluble. The gelatinization of guanylic acid also depends on the presence of a small quantity of sodium or potassium ions. Feulgen later dwelt very exhaustively on the gelatinizing property of the acid sodium salt of guanylic acid. Indeed, Levene and Jacobs in 1912 showed that when the gelatinizing guanylic acid is purified through conversion into the mercury salt, the free guanylic acid obtained from it does not gelatinize but forms a nicely crystalline brucine salt. This investigation of Levene and Jacobs is important for still another reason, namely, it introduced for the first time the method of purification of nucleotides through fractional crystallization of their brucine salts. The method has been in general use since that date," p. 200.

"In 1869 Miescher sent to Felix Hoppe-Seyler, at the time Professor at Tübingen, a manuscript announcing the separation of the nuclear substance from the other constituents of the cells; to this substance he assigned the term 'nuclein'. This discovery was not a matter of mere chance or of good fortune, as discoveries often are, but was the result of conscious and sustained effort to find a chemical explanation of morphological and physiological observations," p. 240.

"The properties of this substance seemed very startling. It had stronger acidic properties than proteins were known to possess. It was soluble in dilute alkalies and insoluble in dilute acids. It was insoluble in water and in organic solvents. In its solubility it resembled mucin but it was not mucin. It did not contain sulfur but did contain a considerable proportion of phosphorus. At the time the only known phosphorus-containing organic component of tissues was lecithin," p. 241.

"Under the influence of Fischer's discovery of glucal, which originally was supposed to possess the property of ordinary aldehydes to restore the color of a fuchsine solution decolorized by sulfurous acid, Feulgen attributed the glucal structure to the sugar of thymonucleic acid. Somewhat later, however, Fischer, Bergmann, and Schotte found that purified glucal does not possess the properties of simple aldehydes and that the reaction attributed to it was due to impurities. This finding naturally disposed of the theory of Feulgen, and accordingly the question arose whether the Schiff reaction obtainable with the neutralized hydrolysate of thymonucleic acid was due to a secondary decomposition product or actually to the sugar present in it. Indeed Steudel and Peiser insisted that both tests discovered by Feulgen were due not to the sugar component but to traces of furfural which were formed on hydrolysis of nucleic acid, and that the sugar itself might be simply glucose, the queer behavior of which could be explained by its firm union with the phosphoric acid," p. 259.

"In 1912, however, Levene and Jacobs stated that in their belief the peculiarities of the conduct of thymonucleic acid were attributable to the unusual instability of the sugar. This has been the firm conviction of the senior writer of this monograph since 1909, for his experiments on plant nucleic acid were always paralleled by experiments on thymonucleic acid. Because of this conviction he initiated in cooperation with Medigreceanu, a detailed study of the nucleoclastic enzymes, and as a result of this investigation it was possible to locate in the intestinal juice an enzyme capable of cleaving nucleotides to the stage of nucleosides only. This finding was the incentive for the work that led finally in 1929 to the isolation of the desoxypentose nucleoside by Levene and London. Through the action of gastrointestinal secretions on a solution of thymonucleic acid, and through the resulting isolation of the nucleosides, the mode of union between sugar and base has been established," p. 264.

"As yet it is not certain whether nucleoproteins are protein salts of nucleic acids or more stable substances derived from nucleic acids through loss of water (esters or acid amides). On this knowledge will depend the significance of the observations of Hammarsten for the biological functions of the cell. It must be admitted, however, that in the fish sperm the nucleic acid is present in an ionizable combination with protoamine," p. 293.

"Proteins with an isoelectric point at pH 4.7 combine with thymonucleic acid more readily in the region of the first two dissociation constants of the acid. This behavior is not easily understandable in view of the fact that the values of the first four dissociation constants of nucleic acids are of the same order of magnitude," p. 293.

"In the preceding chapters reference has been made to the rôle of enzymes in the evolution of the present-day knowledge of the structure of nucleic acids. Needless to say, the chapter on nucleic acids is not the only one in chemistry in which enzymes are employed as chemical reagents. In fact, it is certain that in the future enzymes will be found to be among the most useful reagents in the study of the structure of all natural organic substances of high molecular weight, such as starches, proteins, fats, etc.

"The knowledge of the existence of nucleases antedates our knowledge of the structure of nucleic acids. On the other hand, it is true that it was the elucidation of the structure of ribonucleotides and ribonucleic acids which made possible the identification and the classification of individual enzymes of the group of nucleases. The familiarity with nucleases, in its turn, made possible the elucidation of the structure of thymonucleic acid," p. 309.

Wilder D. Bancroft

Physical Chemistry. *By Louis J. Gillespie. 21 × 14 cm; pp. ix + 287. New York and London: McGraw-Hill Book Company, 1931. Price: $2.75.* In the preface the author says, p. v: "This book has been developed from lecture notes used in a course intended primarily for biological students and given by the author at the Massachusetts Institute of Technology for the past seven years. . . . Certain subjects that are often included in physical chemistry but are not taken up here are modern atomic theory, crystal structure, and photochemistry. There is no chapter on colloid chemistry, but it is believed that most of the important physical chemistry of colloids is presented, the principal omissions being of a descriptive nature. The subject matter has been thus limited in order to make possible a high degree of unity."

The chapters are entitled: introduction—the phase rule—equilibrium in general; a simple theory of gases; general properties of liquids and solids; surface tension; phase relations with liquids and solids for pure substances; relations of gases to liquids or solids when one or more of the phases is a solution; the measurement of vapor pressure—steam distillation; the vapor pressure of liquid solutions; vapor pressure lowering—boiling point elevation—freezing point depression; osmotic pressure; the colligative properties of solutions of electrolytes and of non-electrolytes; electrical conductance; theory of the conduction of electricity through aqueous solutions; transference numbers and the mobility of ions; thermodynamics and free energy; electromotive force and free energy; liquid junction potentials—the activity—the influence of pressure and composition of the electrode substance; chemical cells; cells for the determination of hydrogen-ion concentration or activity; the law of mass action; typical applications of the mass action law in terms of concentrations to electrolytes in solution; amphoteric electrolytes; buffers and titration curves; indicators; Donnan equilibrium, membrane and interfacial potentials; oxidation and reduction potentials; the heat of reaction and the effect of temperature and pressure on chemical equilibrium; the velocity of chemical reactions.

"If a wet soluble salt is placed on a blister, the water is 'drawn out' from the blister. The blister skin is not very permeable to most salts, but is rather rapidly permeated by water, and the water passes out from a dilute solution within the blister to the concentrated solution about the salt. That this might happen, and not the contrary movement of water, we should infer from the fact that the vapor pressure of water in the concentrated solution is less than that in the dilute solution, so that if blister fluid and saturated salt solution were to be placed in separate containers underneath a bell jar, the water would distill from higher to lower vapor pressure", p. 78.

"Physical chemists usually call the osmotic pressure the osmotic pressure of the solution; biologists often call it more explicitly the osmotic pressure of the dissolved substance that cannot pass through the membrane. It is often necessary to be explicit," p. 79.

"The osmotic pressure of the colloids of blood serum has been found to be about 30 to 34 mm. of mercury. In earlier work somewhat lower values were found (25 to 30 mm.). Although the osmotic pressure of the blood has no great significance, it is otherwise with the osmotic pressure of the blood colloids. It is an important task of the kidneys to remove water and many crystalloids from the blood while retaining the albuminous blood colloids. In the glomerulus of the kidney a filtration occurs, in which colloids are retained and water and crystalloids are permitted to pass. The existence of a more or less perfect semipermeable membrane in the glomerulus is evident. Unless the pressure on the blood entering the glomerulus is greater than the osmotic pressure of the blood colloids there will be no tendency for the water to leave the colloids and enter the filtrate. The pressure of the blood is normally ample to account for the filtration. In experiments on animals it has been possible to reduce the blood pressure in the renal artery to a value near the osmotic pressure, and when this is done, the secretion of urine stops.

"The variation in blood pressure from artery to vein is also quite enough to be important in determining the interchange of fluid between blood and lymph," p. 86.

"Because in changes at constant temperature the nature of the intermediate steps is of no importance, there is a definite capacity of a system for doing work in constant-temperature changes of state, which capacity is known as the free energy of Helmholtz, or as the 'work content.' The decrease in this capacity is measured by the maximum quantity of work obtainable in the change of state when conducted throughout at constant temperature.

"When a change of state occurs at constant pressure, work may be done in the expansion of the system against the external pressure. It is proved that its magnitude will be given by the product of the pressure times the increase of volume (and it will be negative, if the volume decreases). This work against constant external pressure depends evidently on the initial and final states alone. Hence, since there is a definite capacity of the system for doing work in constant temperature changes of state, there must be, in the case of changes of state at both temperature and constant pressure, a definite capacity of the system for doing work *in excess of the work of expansion*. This latter capacity is known in America, and to an increasing extent elsewhere, as simply the free energy," p. 123.

"The chloranil electrode is coming into use. The solutions are saturated with both chloranil and its hydroquinone. These two substances do not form an insoluble compound like quinhydrone," p. 167.

"The glass is a glass membrane and very thin, not more than about 0.025 mm. thick. Such membranes were first extensively studied by Haber and Klemenziewicz. Even with the thinnest membranes, an ordinary high sensitivity galvanometer will not receive enough current through the glass membrane to operate satisfactorily, and a quadrant electrometer is generally used, which takes only enough current to charge its plates. Owing to the very high resistance of the cell, the insulation must be extraordinarily effective so that the electrometer does not receive any charge from a source other than the cell. Recently a new vacuum tube has been successfully used to replace the quadrant electrometer.

"Not all glasses are equally suitable. If the glass has a suitable composition and is in contact with solutions not too alkaline it seems to act at both surfaces as an electrode reversible to hydrogen ions alone, that is to say, hydrogen ions are somehow absorbed at one surface and delivered at the other when current is passed without the occurrence of other important changes of state," p. 169. The pH of water is given, p. 199, as 7.45 at 0°, 7.0 at 25°, 6.15 at 100°, and 5.7 at 300°.

"When the electrochemical process does not involve the hydrogen (or hydroxyl) ion, and likewise the chemical reaction, oxidant to reductant, does not involve hydrogen (or oxygen), then the oxidation potential will depend only on the activities of the oxidant and reductant and not upon the activity of hydrogen ion. When the hydrogen ion is involved, it always acts as an oxidant to increase the oxidation potential. Hence, any solution is likely to be less oxidizing at higher pH values.

"It is clear that measurements of oxidation potential should in any case be accompanied by measurements of pH," p. 252.

"In the formulas for oxidation potential the absolute concentrations of oxidant and reductant do not matter but only their ratio. We may have then a given high level of oxidation produced by a large amount of material, or by a small amount. In some biological systems the amount of material responsible for the oxidation potential may be of great importance; for instance, bacteria may in their metabolism use up oxidants and thus greatly change the oxidation potential of the medium, if this is the result of small amounts of material. The oxidation potential does not measure the amount of oxidizing or reducing substance, but only the level of oxidation as defined above," p. 252.

"The investigator in pure physical chemistry has never been interested in measurements of electromotive force unless he has known the electrode processes. The biologist also seeks to learn what are the electrode processes back of an oxidation potential, but can afford to attempt to correlate biological phenomena with oxidation potentials even if without hope of discovering the nature of the electrode processes," p. 253.

On p. 20 there is a helpful table giving the constants in an equation of state for various gases. On p. 82 it is not true in general that the osmotic pressure for two solutes will be the sum of the osmotic pressures of the solutes taken singly. The relation is a function of the solubilities. Few botanists would now admit that osmotic pressure is one of the important factors in the rise of sap in trees, p. 88.

Wilder D. Bancroft

Spektroskopie der Röntgenstrahlen. *By Manne Siegbahn. 24 × 17 cm; pp. vi + 573. Berlin: Julius Springer, 1931. Price: 47 marks, bound 49.60 marks.* In reading the second edition of Siegbahn's "Spectroscopy of X-rays" one has a very vivid impression of the great advances which have been made since the first edition appeared in 1924, and of the way in which the author and his pupils have continued to lead in this field. This is a book which no one but he could have written so well and it immediately takes its place as the standard work on X-ray spectra. The subject has grown so rapidly that the present edition runs to more than twice as many pages as the former. Its pages are packed with information, but the book is very readable because of its excellent arrangement.

The division into chapters follows in the main the lines of the former edition. They comprise I, Knowledge before Laue's discovery of Diffraction; II, X-ray Optics; III, Technique; IV, Emission Spectra; V, Absorption Spectra; VI, Theory of X-ray spectra; VII, Investigation of the Long-wave Region; VIII, The Continuous Spectrum.

The technique of the measurement of X-ray wave-lengths has greatly improved. As is well known, the accuracy with which wave-lengths may be determined in terms of a crystal spacing, and thus compared with each other, is much higher than that with which the crystal constant itself is known, owing to our lack of knowledge of the precise values of atomic constants. It is therefore necessary to define arbitrarily a standard crystal spacing, and refer all X-ray wave-lengths to it. The standard first used was the spacing of planes parallel to the cube face of a rocksalt crystal, which was taken to be primarily $2814.00 \times E$ $(2.81400A)$. Rocksalt is, however, by no means an ideal crystal for the purpose, and the standard now accepted is the spacing of the (111) planes of calcite, defined to be

$$d_{18°} = 3029.04 \times E.$$

As an illustration of the increasing accuracy of measurements we may instance progressive determinations of the iron $K\alpha$ doublet

	K_{α_1}	K_{α_2}
Moseley (1914)	1946	
Siegbahn & Stenstrom (1916)	1932	1928
Siegbahn & Doleysek (1922)	1936.51	1932.30
Lang (1924)	1936.51	1932.38
Larssen (1927)	1935.987	1932.066
Ercksson (1928)	1936.012	1932.076

Whereas in the earlier edition a table of wave-lengths for the K, L, and M series of all elements sufficed to summarize our knowledge, so much work on emission spectra has now been done that it is found desirable to accord each element a table of its own. The chapter on emission spectra has been expanded to four times its former size.

Certain sections of the book are entirely new, and describe lines of investigation which have been developed since the first edition was written. Most of the familiar optical effects of surface reflection, of refraction, and of diffraction have now been paralleled in the X-ray region. The existence of a refractive index for X-rays slightly less than unity was predicted by Darwin in 1914, and Compton discovered the consequent total external reflection at a plane surface. The dispersion, or variation of refraction index with wave-length, shows interesting abnormalities in the neighbourhood of an absorption edge which are analogous to optical anomalous dispersion. The refraction of X-rays by a prism, their diffraction by passage through a fine slit, fringes by the Lloyds mirror method, and fringes by reflection at both surfaces of a thin film, have all been observed. Most important of all, the diffraction of X-rays by a ruled grating, first demonstrated by Compton and Duane, has been used by Siegbahn and his School and by other workers to investigate the range between the X-ray and optical regions with conspicuous success. Chapter VII is devoted to this new field. Spectra recently obtained with a curved grating and fine angle of incidence show a wealth of detail in the region 50 A to 500 A which recalls that of optical spectra. It is now possible to make precision measurements in the whole range of wave-lengths, the former gap between X-rays and light having been completely bridged.

Other new sections deal with the fine structure of absorption edges, the influence of chemical combination on absorption and emission spectra, the fine structure and breadth of emission lines.

A series of tables are given, of which the most important is a list of the strongest lines arranged in order of wave-length. The extensive literature-index occupies eighty pages, in itself an indication of the vast field which is reviewed. There are separate indices for authors and for subjects.

One cannot but be grateful that Professor Siegbahn has found it possible, while engaged so actively in research, to bring up to date his exposition of a subject in which he is so great an authority.   *W. L. Bragg.*

Fortschritte der Metallkunde und ihre Anwendungen auf Leichtmetalle: (*A Symposium*). *29 × 20 cm; pp. vi + 353. Berlin: Verlag Chemie, 1931. Price: 16 marks.* The title of this publication suggests a volume of delicious reading for the metallurgist, and the presence of such names as Sachs, Mark, Masing, and Polanyi in the author-index serves to enhance the prospect. The book consists however, of 67 miscellaneous papers contributed to the 36th Congress of the Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie E. V., of which only about 30 would seem to be directly related to the formula which appears on the cover. "Advances in Physical Metallurgy and their application to the Light Metals" might pass as a translation of the general subject of the Congress, though it must be admitted that a difficulty has been generally recognised in rendering into English the word "Metallkunde." Suggestions which have been advanced quite recently to replace the term used above, include such words as "metallics," "metallosophy" and "metal-lore." Whatever equivalent the English metallurgist might concoct for purposes of translation, however, the general sense of the title would not suggest to him that papers on "The Cyclohexane Problem," "The Electron Structure of Nitrogen Peroxide" or "The Thermo-dynamics of the Nitrogen Oxygen Combination" would find shelter within the covers. Yet here they are in considerable numbers, and doubtless many of them will be of great interest to the physical chemists.

With this preliminary observation it may now be said that the book contains important metallurgical contributions. The text is suitably illustrated with photographic reproductions and diagrams, and each article is followed by such discussion as it provoked at the meeting. The papers are grouped into ten classes, the first five of which—covering 150 pages—contain most of the metallurgical matter. The remainder deal with spectra and molecular structure; general physical chemistry; surface chemistry, kinetics and photo effects; electrolytes; and finally electrochemistry. In these latter classes a few papers dealing with corrosion and electrodeposition are to be noted. A short account of the chromium-plating of light alloys by A. Koenig produced a considerable discussion, but as a protection against corrosion this treatment is probably not as satisfactory as the well known anodic oxidising process dealt with in a paper by H. Röhrig. The large-scale production in recent years of aluminium of 99.95 per cent purity prompted M. Centnerszwer to investigate its behaviour towards various acids and alkalies at different temperatures and concentrations. The results here recorded shew that the very pure metal is much more resistant to solution than that of "commercial" purity, especially in the case of $N/2$ HCl.

In the metallurgical section proper, a certain amount of the work deals with such solid-solutions as those of Au-Cu which precipitate intermetallic compounds on slow cooling. Thus Masing introduces them into his paper on the precipitation-hardening of alloys; Vogt into a study of magnetic susceptibility measurements of metals and alloys; whilst Eisenhut and Kaupp report upon their examination by the electron-diffraction procedure. This new method has yielded results which in some respects compare favourably with X-ray diffraction tests. Lattice distortion in alloys like duralumin which undergo age-hardening, is dealt with by Hengstenberg and Mark, X-ray intensity measurements being made at various times after quenching to obtain particulars of the reflection behaviour of the lattice. Recrystallisation phenomena are treated by Beck and Polanyi, and by Tammann, whilst von Hevesy and Seith's account of diffusion in metals concludes that the process is unilateral and not mutual.

With the continued development of light alloys, papers dealing with magnesium are to be expected. The purification of this metal by vacuum distillation is described by Kaufmann and Siedler, and a technological article on "Elektron" alloys is contributed by W. Schmidt. A detailed study of the physical properties and metallography of magnesium is provided by E. Schmid, particulars being given of its binary alloys with Al, Zn, and Mn, together with the deformation of single crystals of the metal. New work upon this latter subject is not so much in evidence just now as it was a few years ago, but Goens and Schmid contribute a paper on "Elasticity investigations of iron crystals." Nothing is devoted specially to beryllium, but Masing introduces the Be-Cu alloys into his article on age-

hardening, showing that after 81 hours the Brinell hardness number of one of them will rise from 110 to 360.

These references to some of the papers will serve as an indication of the subjects represented in this publication. The light metals and alloys have brought with them many new problems—as is made evident here by an excellent survey by G. Sachs—but the study of these problems has already produced a rich yield of useful results.   *Hugh O' Neill.*

Recent Advances in Physical Chemistry. *By Samuel Glasstone. 14 × 22 cm; pp. viii + 470. London and New York: J. & A. Churchill in P. Blakeston's Son & Co., 1931. Price: 15 shillings.* This text-book will be appreciated by teachers of physical chemistry at the Universities, for it covers a much wider range of subjects than can be dealt with adequately in university lecture courses to undergraduates. It can be used with advantage to supplement the information given in such courses.

Among the topics discussed are the electronic theory of valency, dipole moments, molecular spectra, homogeneous and heterogeneous reactions, photochemical reactions, solubility, and strong electrolytes, and a very useful list of references is given at the end of each chapter. The author has made a wide survey of the literature, and there is little that has escaped his net. There are, however, two topics missing that might have been dealt with in a work of this kind, viz. the solid state, and recent advances in thermodynamics.

The mode of treatment on the whole is qualitative and there is no great depth of penetration. Equations are given, but no attempt is made to give an explanation of their physical basis. For example, the theory underlying the activation of gaseous molecules by collision is not given in the chapter on homogeneous gas reactions, although this theory is essential if students are to gain a proper grasp of what is actually happening in gaseous reactions. The book is also open to the serious criticism, that the author has devoted too much space to subjects already dealt with in monographs published in English. It is very largely, although not entirely, a text book compiled from monographs. There is too much space devoted to the approximate and elementary theories of valency and too little attention paid to ideas based on the newer advances of physics.

In spite of these faults, which seriously affect its value as a text-book for advanced students, it will prove a valuable addition to the libraries of teachers of chemistry in schools and to those chemists who wish to be informed of the present trend of chemical research.

The book is interesting to read, and is well illustrated by suitable diagrams.

W. E. Garner.

The Colorimetric and Potentiometric Determination of pH. Electrometric Titrations. *By I. M. Kolthoff. 23 × 15 cm; pp. xi + 167. New York: John Wiley and Sons, 1931. Price: $2.25.* This book is a condensed outline of the material contained in the author's other publications on Potentiometric Titrations and Konduktometrische Titrationen. It is intended as a text for a special advanced course in analytical chemistry to familiarize the student with these important methods and to enable him to apply them to his own special problems of research.

The book includes chapters on (1) Acids and bases, the reaction of aqueous solutions; (2) Indicators; (3) The colorimetric measurement of pH; (4) Electrode potentials; (5) The technique of potentiometric measurements; (6) The potentiometric measurement of the hydrogen ion activity; (7) Potentiometric titrations; (8) Conductometric titrations; and (9) An outline for a practical laboratory course of instruction.

The theory involved is given very briefly and there is the possible criticism that many of the points such as salt effect, protein effect, indicator theory and the conversion of hydrogen ion concentration to pH, are inadequately covered. However the author gives references to the places where a more comprehensive treatment of most of these points may be found. Problems are introduced at the end of the chapters to illustrate the fundamentals discussed.

The book was written "with the idea of offering an introduction to the above fields without claiming in any way an exhaustive treatment," and the study of the theory given and the completion of the laboratory course should serve admirably to give the student an adequate knowledge of these methods.   *M. L. Nichols.*

IONIZATION PRODUCED BY RADON IN SPHERICAL VESSELS

BY GEORGE GLOCKLER AND G. B. HEISIG

Introduction

The usual methods of calculating the ionization produced by the alpha-particles from Rn, RaA, and RaC in spherical vessels[1] assume the validity of Geiger's two-third power law ($I = kr^{2/3}$). Some evidence was obtained in connection with other calculations made by the authors that the Geiger Law does not hold rigidly when the usual ranges of the alpha-particles are used. Since the publication of the above paper some question as to the validity of the law was also raised in the report of the International Radium Standards Committee.[2] In the present paper a study is made of the assumption that Geiger's Law is applicable in the calculation of the ionization produced by the alpha-particles from Rn, RaA, and RaC which are used to cause the chemical effects studied by Lind,[3] co-workers and others.

The following terms are used in this paper:

I_T = Total ionization produced by an alpha-particle in its path.

k = Proportionality factor in Geiger two-thirds power law for Rn at $20° = 6.478 \times 10^4$

k' = Proportionality factor for RaA = 6.417×10^4

k'' = " " " RaC = 6.253×10^1

r = Range of an alpha particle from Rn

r' = " " " " " for RaA

r'' = " " " " " for RaC

r_o = 3.45 cm = concordant range for alpha-particles from Rn at $0°$ and 76 cm.

p = Path traversed by an alpha particle

I_p = Ionization cm^{-1} at the point p

ρ = r/R

I_1 = Ionization from an alpha particle from Rn

I_2 = " for alpha particles from RaA gas

I_3 = " " " " " RaC gas

I_4 = " " " " " RaA on the wall

I_5 = " " " " " RaC on the wall

F_1 = Efficiency factor for Rn

F_2 = " " " RaA in the gas phase

F_3 = " " " RaC in the gas phase

F_4 = " " " RaA on the wall

F_5 = " " " RaC on the wall

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[1] Glockler and Heisig: J. Phys. Chem., **35**, 2478-2491 (1931) where other references will be found.

[2] Rev. Mod. Phys., **3**, 431 (1931); J. Am. Chem. Soc., **53**, 2441 (1931).

[3] "The Chemical Effects of Alpha Particles and Electrons" (1928).

A $= k'/k = 0.99058;$ $B = k''/k = 0.96527$

v $=$ velocity of an alpha particle

a_0 $=$ constant in $v^3 = a_0 r$

a $= r'/r = 1.165;$ $b = r''/r = 1.783$

N $=$ Number of alpha particles $=$

$$E_0(1-e^{-\lambda t}) \times \frac{3.70 \times 10^{10}}{2.097 \times 10^{-6}} = E_0(1-e^{-\lambda t}) \times 1.764 \times 10^{16}$$

R $=$ Radius of the vessel

s $=$ Stopping power of a gas

P $=$ Pressure of the gas

t $=$ Temperature in degrees C

g $=$ Specific ionization of a gas

F' $=$ Efficiency factor based on decomposition of 70% of RaA and 93% of RaC on the wall.

I. *The Geiger two-third power law.* This important relation connects the ionization produced in the part of the path traversed by an alpha-particle and its range. The law is:

$$I_T = kr^{2/3} - k(r-p)^{2/3} \tag{1}$$

If it is desired to calculate the ionization cm^{-1} at a given distance from the origin of the alpha-particle equation (1) may be written:

$$I_T = \frac{dI}{dp} = 2/3 \frac{kr^{2/3}}{r(1-p/r)^{1/3}} \tag{2}$$

Equation (2) permits the calculation of values which enable a theoretical ionization curve for alpha particles to be constructed similar to those obtained experimentally.

The first question which arises has to do with the definition of the range of a single alpha-particle and with the average range of a group of such particles.

II. *The range of a single alpha particle.* 1. Curie[1] has attempted to determine the ionization curve of a single alpha particle from the Bragg-curve obtained from a canalized beam. She states[2] that the ionization curve of a single alpha-particle differs very little from the curve of Bragg. G. H. Briggs[3] calculated the "mean" range for a "group" of alpha-particles from the data of Curie for a single one and found that the mean range at 15°C and 760 mm. in air is 6.90 cm. and the extrapolated range under the same conditions was 6.96 cm. I. Curie and Mercier[4] determined the mean range by the Wilson cloud method to be 6.92 cm. at 15°C and 760 mm. air uncorrected for pressure of water vapor. Geiger[5] determined the ranges of the alpha particles from many radioactive bodies for a canalized beam of such particles. These values for the

[1] Ann. Phys., (10) 3, 299-401 (1925).

[2] Loc. cit. page 400.

[3] Proc. Roy. Soc., 114 A, 341-354 (1927).

[4] J. Phys., 7, 289 (1926).

[5] Z. Physik, 8, 45-57 (1922).

ranges are determined for a group of alpha-particles and give therefore the range for an average one. It is seen then that the range of a single alpha-particle and that of a group of them differs very little and no distinction is made in the following considerations between these two ranges since their numerical values are not greatly different. The various definitions of "range" will now be considered.

III. *The extrapolated range.* The ionization curve for an alpha-particle of RaC has, towards the end of the range, a small tail which is due to straggling and a few particles of especially long ranges. This section of the ionization curve depends upon the sensitivity of the detecting apparatus and the intensity of the source and cannot be determined accurately. However, the descending portion of the curve after the maximum of ionization is a straight line and when extended cuts the abscissa at a well defined point. This point determines the "extrapolated range."[1]

Geiger states that this extrapolated range is a definitely reproducible quantity and attempted to state the two-third power law using this extrapolated range. However he found[2] that the use of this range did not give a theoretical curve concordant with the experimental one. He used an average range and found that the two-third power law and experiment checked fairly well in the case of RaC. This average range is very nearly equal to the distance from the source to the point at which maximum ionization occurs. Grieger did not study the detailed ionization curves for the alpha-particles from RaA and Rn. When it is attempted to apply the two-third power law (eq.2) to the case of RaA and Rn using the extrapolated ranges, the theoretical curves do not fit the experimental ones of Henderson[3] as can be seen from Fig. 1 which is based on the data in Tables I and II.

TABLE I

Ionization per cm. path for RaC*. Experimental Values from Henderson
(loc. cit.) $I_T = 2.20 \times 10^5$ Ion pairs

Range 20° 76 cm. air (cm.)	Ion pairs per cm. $\times 10^{-4}$	Range 20° 76 cm.	Ion pairs per cm. $\times 10^{-4}$
0	2.09	6.44	6.29
1.07	2.25	6.55	6.68
2.15	2.48	6.59	6.70
3.22	2.77	6.65	6.54
4.29	3.23	6.76	6.01
5.37	4.01	6.87	4.51
5.90	4.83	6.98	2.15
6.33	5.89	7.08	0.29
		7.19	0.00

* Note: The experimental curves for ionization per cm. path for RaA and Rn can be obtained from the curve for RaC by shifting the RaC curve a distance 2.29 cm. (= 7.092 − 4.084 cm.) and 2.90 cm. (= 7.092 − 4.193 cm.) to the left, respectively, for RaA and Rn.

[1] Marsden and Perkins: Phil. Mag., **27**, 690 (1914).
[2] Proc. Roy. Soc., **82 A**, 486 (1909); **83**, 505 (1910).
[3] Phil. Mag., **42**, 538-551 (1921).
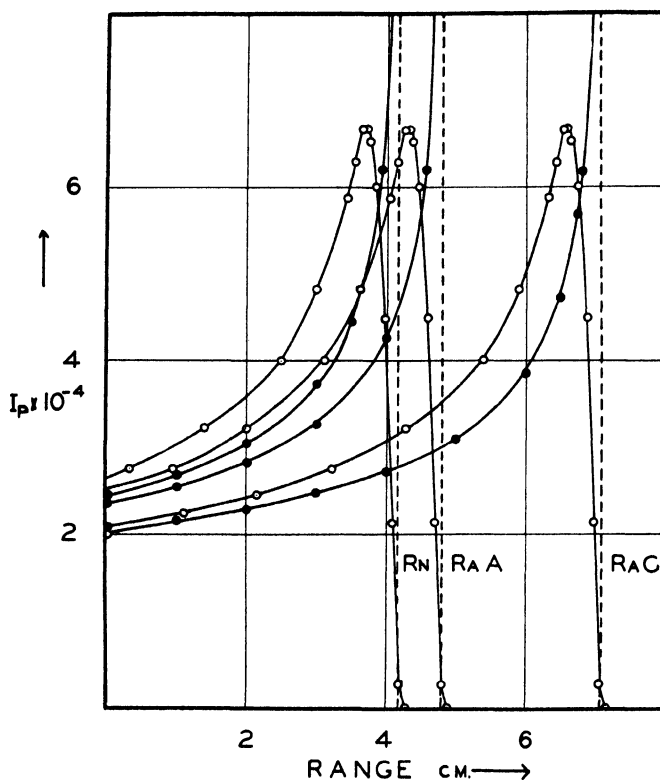
FIG. 1

Geiger Law of Ionization per cm. path as a function of the extra-
polated ranges for Rn, RaA and RaC. (o) experimental values; (●)
calculated values

TABLE II

Ionization per cm. $\times 10^{-4}$ for alpha-particles from RaC, RaA and Rn,
calculated by means of equation (2) on the basis of 2.2×10^4
ions pairs for RaC

p	Extrapolated Ranges Fig. 1			Empirical Ranges Fig. 2		
	RaC	RaA	Rn	RaC	RaA	Rn
0.00	2.07	2.36	2.46	2.22	2.53	2.65
1.00	2.18	2.55	2.70	2.34	2.75	2.92
2.00	2.31	2.82	3.06	2.51	3.08	3.36
3.00	2.48	3.27	3.75	2.71	3.66	4.31
3.50	—	—	4.49	—	—	5.64
4.00	2.73	4.28		3.02	5.32	
5.00	3.11			3.55		
6.00	3.86			4.93		
6.50	4.74			8.97		
6.75	5.69					
6.83	6.19					
7.00	8.87					

TABLE II (Continued)

Concordant Ranges
Fig. 3

p	RaC	RaA same k	RaA diff. k	Rn same k	Rn diff. k
0.00	2.22	2.55	2.63	2.70	2.79
1.00	2.34	2.73	2.87	3.00	3.10
2.00	2.51	3.14	3.24	3.50	3.62
3.00	2.71	3.79	3.91	4.70	4.86
3.50	—	—	—	7.13	7.37
4.00	3.02	6.12	6.31		
5.00	3.55				
6.00	4.93				
6.50	8.97				
6.75					
6.83					
7.00					

The extrapolated ranges at 20°C and 760 cm. air are 7.09 cm., 4.80 cm. and 4.19 cm. for RaC, RaA and Rn respectively. The total ionizations I_T are:

$$2.2 \times 10^5,\ 1.70 \times 10^5 \text{ and } 1.55 \times 10^5 \text{ ion pairs}$$

for RaC, RaA and Rn respectively. The values are taken from the report of the International Radium Standards Commission. In order to obtain concordant experimental and theoretical curves for the ionization as a function of the range, it is necessary to use an empirical range as was suggested by Geiger.

IV. *The empirical range.* When the experimental ionization curves for RaC obtained by Henderson are used for a comparison with the Geiger law, it is found that an empirical range of 6.6 cm. (76 cm. air, 20°) will give a good fit between the experimental ionization curve and the curve obtained by the use of the theoretical two-thirds power law. This range is called the "empirical" range. Since this empirical range is made to fit the Geiger law, the constant k involved in the expression:

$$I_T = k'' \times r''^{2/3} \tag{3}$$

can be easily calculated. Since the International Radium Standards Commission recommends the value of $2.2 \times 10^5 = I_T$ obtained by Fonovits-Smereker[1] this value will be used in these calculations.

Then from Eq. (3):

$$k'' = 6.253 \times 10^4$$

The corresponding empirical ranges for RaA and Rn are defined as follows: The constant k is supposed to apply in all three cases and the total ionizations for RaA and Rn are taken from the report cited above. Then

For RaA: $1.70 \times 10^5 = 6.253 \times 10^4 \times r'^{2/3}$
For Rn: $1.55 \times 10^5 = \ '' \ \times r^{2/3}$

[1] Wien. Ber., **131**, 355 (1922).

and the empirical ranges are found to have the values

$$r' = 4.47 \text{ cm and } r = 3.90 \text{ cm. } (20° \text{ and } 76 \text{ cm. air})$$

When, however, these ranges and values of the total ionizations are used to obtain the detailed ionization curves for Rn and RaA, it is again found that they do not produce a set of curves that fit the experimental ones satisfactorily as is seen from Fig. 2 which is obtained by the use of Tables I and II.
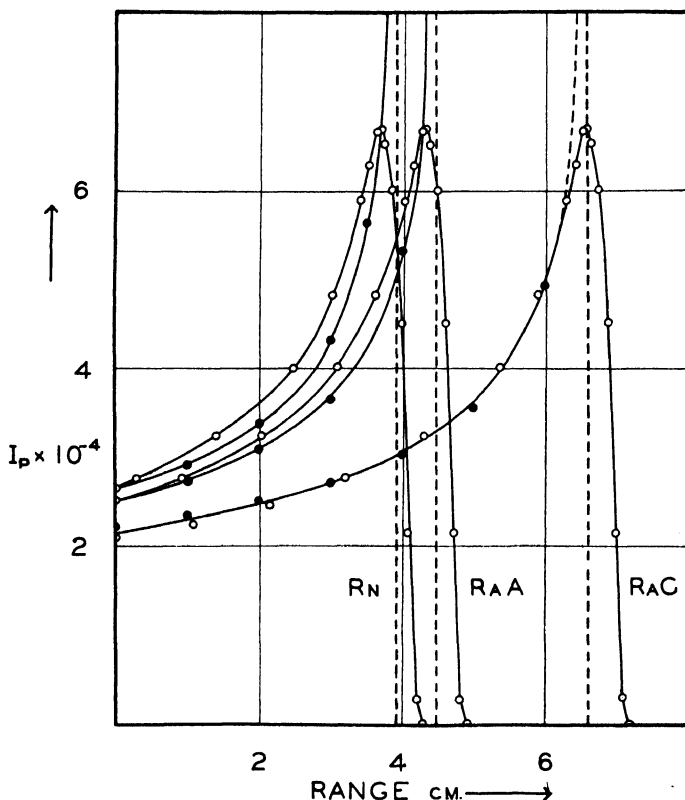
Fɪɢ. 2

Geiger Law of Ionization per cm. path as a function of the empirical ranges for Rn, RaA and RaC. (o) experimental values; (●) calculated values

The difficulty is due to the attempt to produce a set of ionization curves which will give the proper total areas at ranges which are incompatible with the equations.

V. *The concordant range.* A satisfactory set of ranges for RaC, RaA, and Rn may be defined by making the difference between them and the extrapolated ranges a constant. This procedure seems to be justified because the ionization curves for the three sets of alpha particles are treated in a like manner towards the end of the respective ranges.

TABLE III

	RaC	RaA	Rn
Extrapolated Range, 20°, 76 cm. air	7.092 cm.	4.804 cm.	4.193 cm.
Constant difference:	.492 "	.492 "	.492 "
Concordant range, 20°, 76 cm. air	6.60 cm.	4.312 cm.	3.701 cm.
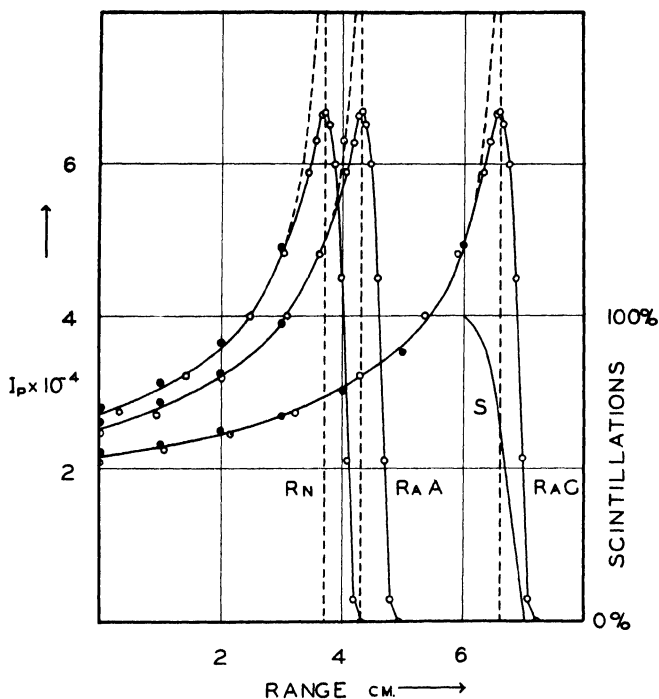
FIG. 3

Geiger Law of Ionization per cm. path as a function of the concordant ranges for Rn, RaA and RaC. (o) experimental values; (●) calculated values. S = the fractional decrease in scintillations near the end of the range for RaC

These ranges are again based on 6.6 cm. for RaC and are called "concordant" ranges. They give ionization curves which fit the experimental curves, as is seen in Fig. 3. The data are obtained from Tables I and II. However, the total ionizations for RaA and Rn do not now agree with the accepted values obtained by the use of the extrapolated ranges, if the same constant k is used in the three cases:

$$k \times r''^{2/3} = 6.253 \times 10^4 \times 6.60^{2/3} = 2.2 \times 10^5$$
$$k \times r'^{2/3} = \text{''} \times 4.312^{2/3} = 1.66 \times 10^5 \text{ (instead of 1.7} \times 10^5)$$
$$k \times r^{2/3} = \text{''} \times 3.701^{2/3} = 1.50 \times 10^5 \text{ (instead of 1.55} \times 10^5)$$

VI. *Empirical constants.* Agreement in the total ionizations and close-fitting detailed ionization curves can be obtained by the use of an empirical set of curves of the type of the Geiger $\frac{2}{3}$ power law if the constant of the equation is taken to be different for each set. These empirical constants are obtained by using the total ionizations for RaA and Rn (secured by the use of the extrapolated ranges from RaC) and the concordant ranges.

For RaC
$$k''r''^{\frac{2}{3}} = 6.253 \times 10^4 \times 6.60^{\frac{2}{3}} = 2.2 \times 10^5 \tag{4}$$

$$\text{or } I_p = \frac{dI}{dp} = \frac{2}{3} \cdot \frac{2.2 \times 10^5}{6.6 (1 - p/6.60)^{\frac{1}{3}}} \tag{5}$$

For RaA:

$$k'r'^{\frac{2}{3}} = 6.417 \times 10^4 \times 4.312^{\frac{2}{3}} = 1.70 \times 10^5 \tag{6}$$

$$\text{or } I_p = \frac{dI}{dp} = \frac{2}{3} \cdot \frac{1.70 \times 10^5}{4.312 (1 - p/4.312)^{\frac{1}{3}}} \tag{7}$$

For Rn

$$k\,r^{\frac{2}{3}} = 6.478 \times 10^4 \times 3.701^{\frac{2}{3}} = 1.55 \times 10^5 \tag{8}$$

$$\text{or } I_p = \frac{dI}{dp} = \frac{2}{3} \cdot \frac{1.55 \times 10^5}{3.701 (1 - p/3.701)^{\frac{1}{3}}} \tag{9}$$

There is then possible a choice in method: Either the same value for $k (= 6.253 \times 10^4)$ may be used for the calculation, leading to total ionization values of 2.2×10^5, 1.66×10^5, 1.50×10^5 for RaC, RaA and Rn respectively or different values of k may be used, namely,

$$k'' = 6.253 \times 10^4, k' = 6.417 \times 10^4, \text{ and } k = 6.478 \times 10^4$$

for RaC, RaA and Rn respectively. These latter values give the total ionization 2.2×10^5, 1.70×10^5 and 1.55×10^5 respectively for RaC, RaA, and Rn, which values agree with the total ionization obtained graphically by the use of the extrapolated ranges and the experimental value for RaC.

With either method close fitting detailed ionization curves are obtained. The graphs of Fig. 3 represent the situation in either case on the small scale used in preparing these curves.

The reason that with the same value of k and the concordant ranges the total ionizations for RaA and Rn do not agree with the values obtained graphically from the extrapolated ranges and the experimental value of ionization for RaC, must lie in the fact that the concordant ranges are defined in an empirical manner.

Since, however, the present considerations aim to calculate the ionization produced by Rn it seems logical to accept the values for the total ionizations for RaA and Rn as obtained from the extrapolated ranges from RaC. In other words it appears proper to use different k values. This situation does not agree with the usual view that the alpha particle from different sources is the same but for its velocity of emission from the radioactive body. On this basis it would be expected that the quantity k is a constant for different alpha particles. However as far as is known experimentally the law $v^3 = a_0 r$ is not

completely verified in as much as the constant a_0 varies for alpha particles from RaC, ThC and Po.[1]

On this basis it does not seem impossible that k may also vary for different alpha particles.

Ionization for the three sets of alpha particles for Rn shall then be calculated with the values of k as follows:

$$RaC: k'' = 6.253 \times 10^4$$
$$RaA: k' = 6.417 \times 10^4$$
$$Rn: \ k \ = 6.478 \times 10^4$$

and the total Ionizations

$$RaC: I_T = 2.20 \times 10^5$$
$$RaA: \ \ \ = 1.70 \times 10^5$$
$$Rn: \ \ \ \ = 1.55 \times 10^5$$

It is quite necessary that the many definitions of range be kept clearly in mind and for this purpose Table IV gives the values for these ranges.

For the purpose of calculating the ionization in chemical experiments with vessels of average size (.5-5 cm. radius) it is important that the proper range be used in these calculations. Evidently the range chosen should be the one that will give results closest to the theoretical Geiger ⅔ power law. This range is the concordant range defined above.

TABLE IV .

Ranges of Alpha Particles from Rn, RaA and RaC
at 20° and 76 cm. air

	Extrapolated Ranges	Empirical Ranges	Concordant Ranges
Rn	4.19	3.90	3.70
RaA	4.80	4.47	4.31
RaC	7.09	6.60	6.60

While the concordant ranges will give the best fit to the ionization curves and for this reason their use is justified, there is also experimental justification for their use (curve S in Fig. 3). Geiger[2] has shown that the scintillations from RaC at the end of the range decrease in number. This shows that the alpha-particles straggle, i.e. that they have somewhat different ranges. In the case of RaC, 15°C, 76 cm. at about 6 cm. from the source, the number of scintillations begins to decrease. From these observations, it is possible to deduce an average range as is shown in Fig. 3 of 6.76 cm. at 20°C, 76 cm. in air. The concordant range chosen to give the best fit for the theoretical and experimental ionization curves of alpha particles from RaC was 6.6 cm.

If the Geiger equations 4-9 containing different constants for RaC, RaA and Rn are not used, it becomes necessary to establish completely empirical relations which would be more complicated. Such a procedure does not seem necessary or desirable for the present purpose.

[1] Report Int. Radium Standards Commission: loc. cit. page 431.

[2] Proc. Roy. Soc., **83 A**, 511 (1910).

VII. *Efficiency Factors.* The use of the concordant ranges in the expression of the Geiger Law and the change from 2.37×10^5 ion pairs for RaC to the value 2.2×10^5 cause a small change in the efficiency factors. These factors have been recalculated for the case that 70% RaA and 93% RaC are decomposed on the wall and are given in Table V. The equations of Mund[1] have been used. The change from large to small spheres occurs at $\rho = 2$, for Rn; at $\rho = 1.72$ for RaA and at $\rho = 1.12$ for RaC.

The total ionization is given by

$$I_T = I_1 + I_2 + I_3 + I_4 + I_5$$

where

$$I_1 = N \, kr^{2/3} \, F_1$$

for decomposition in the gas phase.[2]

The ionization produced by RaA and RaC in the gas phase is respectively,

$$I_2 = .3 \times N \times k \times r^{2/3} \times A \times a^{2/3} \times F_2$$

and

$$I_3 = .07 \times N \times k \times r^{2/3} \times B \times b^{2/3} \times F_3$$

The factors F_2 and F_3 are obtained from the work of Mund. The ionization produced by RaA and RaC on the wall is obtained from

$$I_4 = .7 \times N \times k \times r^{2/3} \times A \times a^{2/3} \times F_4$$
$$I_5 = .93 \times N \times k \times r^{2/3} \times B \times b^{2/3} \times F_5$$

where the factor F_4 and F_5 are gotten from Mund's equation (3). The concordant ranges were used (Table III).

TABLE V

Efficiency Factor to be used in calculating Ionization produced by Alpha Particles from Radon in Spherical vessels

ρ	F'	ρ	F'	ρ	F'
0.0	2.472	1.4	0.974	4.0	0.297
.1	2.353	1.5	.901	5.0	.235
.2	2.235	1.6	.836	10.0	.116
.3	2.117	1.7	.777	15.0	.077
.4	2.000	1.8	.723	20.0	.057
.5	1.884	1.9	.676		
.6	1.771	2.0	.636		
.7	1.657	2.2	.571		
.8	1.546	2.4	.517		
.9	1.437	2.5	.494		
1.0	1.331	2.6	.473		
1.1	1.232	2.8	.436		
1.2	1.140	3.0	.404		
1.3	1.053	3.5	.342		

Table V gives sufficient information so that a large scale plot of F' as a function of ρ can be made from which any corresponding set $(F'\rho)$ can be

[1] J. Phys. Chem., **30**, 890-894 (1926).

[2] Mund: loc. cit., eq. (1).

obtained. Interpolation of the values given in Table V is not satisfactory because the relation between F′ and ρ approaches in shape a hyperbola.

VIII. *Calculation of Ionization.* The calculation of ionization is to be made as follows:

Consider a vessel of 2.232 cm. radius filled with acetylene at 599 mm. at a temperature of 25°C. The concordant range of the alpha particles from Rn is calculated as follows:

$$r = \frac{r_0}{s} \times \frac{760}{P} \times \frac{273 + t}{273}$$

where r_0 = 3.45 cm = concordant range of Rn at 0°, 76 cm. air.

  s = stopping power = 1.12 for C_2H_2.

Then r = 4.27 cm. and $\rho = \dfrac{4.27}{2.232} = 1.913$

From a plot of F′ as a function of ρ it is found that the desired value of F′ is .671 which yields for the total ionization of N alpha particles:

$$
\begin{aligned}
I_{T, C_2H_2} &= N \times g \times kr^{2/3} \times F' \\
&= N \times 1.26 \times 1.55 \times 10^5 \times .671 \\
&= 1.3105 \times N
\end{aligned}
$$

Summary: The assumption that the Geiger Law for ionization by the alpha particles from Rn holds when using the extrapolated ranges is shown to be inadequate. It is necessary to use empirically defined ranges as has been done by Geiger for RaC. While it is then possible to fit a $\frac{2}{3}$ power law to the ionization curve for an alpha particle from RaC, the two other curves for RaA and Rn cannot be made to coincide with the known experimental curves. In order to obtain close-fitting two-third power curves for all three sets of alpha particles it is necessary to define empirically a set of three ranges called the concordant ranges. If now a fixed value of k ($= 6.253 \times 10^4 =$ the constant in Geiger's $\frac{2}{3}$ power law) is used for all three sets of alpha particles, then the total ionizations for RaC, RaA and Rn are: 2.2×10^5, 1.66×10^5, and 1.50×10^5 which values do not agree with the total ionizations obtained from the extrapolated ranges which are: 2.2×10^5, 1.70×10^5 and 1.55×10^5. These latter values can be used if different values of k are taken: 6.253×10^4, 6.417×10^4 and 6.478×10^4, respectively for RaC, RaA and Rn. With these changes it is possible to obtain three curves for RaC, RaA and Rn which fit the experimental ones. The efficiency factor for the calculation of ionization for the case that 70% RaA and 93% RaC decompose on the wall have been calculated. The concordant ranges, and the proper constants giving the total ionizations as obtained graphically from the ionization curve for RaC and the experimentally determined extrapolated ranges have been used. The other method of calculation would demand the use of the same constant (k = 6.253×10^4) and values for the total ionization for RaA and Rn which differ from the above. This last method would give efficiency factors differing from the adopted set by about 1%.

University of Minnesota,
Minneapolis, Minn.
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THE FADING OF DYES AND LAKES

BY JOHN W. ACKERMAN

Introduction

Since early times man has been interested in color, for we have accounts that show that the kings or ruling classes were the only ones allowed to wear pronounced colors like scarlet and purple; and the known globe was scoured for rare and pleasing colors. Tyrian purple was called the royal purple and used only by kings in their court ceremonials. The early colors were made from natural things, and it was found that they would dye not only cloth, but also would set or mordant with certain earths, which were themselves natural products, and this is the origin of dyeing as we know it today. Even now we find that some of these colors have carried through, such as ochre, umber and sienna. Mosses were used and even secretions of sea animals like the squid for making sepia.

Although colors were known and used in ancient days, the person of average means was unable to buy them because of their high cost. This was decreased with the introduction of synthetic dyes, but it was not until 1856 that William Perkin obtained the first coal-tar dye. Since that time practically all the natural coloring matters have been obtained in the laboratory and many more new dyes. However, the extensive use of color has developed comparatively recently. Not only do we have brightly colored clothes and illustrations in magazines, but also in the last few years colored automobiles, kitchen utensils, furniture, tile, linoleum, cameras and now colored factories. This great increase in the use of color has naturally led to the desire for dyes that are fast—to light, washing, rubbing and weathering; but it is only the first of these in which we are interested.

One of the first indications of the action of light were the laws enunciated by Grotthuss in 1818: (1) Only those rays of light which are absorbed can produce chemical action. (2) The action of a ray of light is analogous to that of a voltaic cell. Not much more was accomplished until the latter part of the last century, since the chemists were more concerned with compounds that would yield color and not so much with the properties.

In 1894 Dufton[1] claimed that there were three factors responsible for the decomposition of colors—light, oxygen and water. "Light is the most important factor, for it will decompose some [colours] in the absence of air and moisture. The fading of colours is due more particularly to the visible portion of the solar radiation, and the rate of fading is not simply a function of the wave-length of incident light but depends on the colour of the material exposed. The fading is brought about by the absorbed rays; each colour being affected the most by those rays which it absorbs the strongest."

[1] J. Soc. Dyers Colourists, **10**, 90 (1894).

At the same time it was shown[1] that the fading of methylene blue may result from oxidation or reduction but it is usually an oxidation because of the oxygen of the air. Later Gebhard[2] explained that in the presence of gelatin or of stronger reducing agents the bleaching of methylene blue by light is due to a reduction.

There was very little theory to show why colors faded, although Brownlie[3] claimed that the action of light on dyed fabrics is a direct interaction of the color with the oxygen of the air and with any ozone or hydrogen peroxide present to form colorless substances of unknown composition, and that the action is proportional to the moisture present.

"The action of light[4] may be divided into two classes—photo-chemical and photo-physical. In the first case it is assumed that a direct action takes place which involves the re-arrangement in the molecule itself, and in the second that the action is said to be equivalent to the polymerization of formaldehyde. The theories for the fading are:—

(1) *Oxygen Theory*—Dyes under the influence of light interact with oxygen and form colourless compounds. The colour at the end of the exposure is proportional to the resistance of this reaction.

(2) *Ozone Theory*—Colours are decomposed or altered by the production of ozone or hydrogen peroxide in the fiber, chiefly by the evaporation of moisture.

(3) *Reduction Theory*—The dye is reduced by the cotton fiber or directly by the action of light.

"Under the influence of light vibrations, the oxygen molecule may be more readily split up $O_2 \rightleftarrows O + O$ and this takes place more readily when the oxygen is associated with water molecules. The general conclusion is that the action is an oxidizing one and not a reducing one. In the absence of oxygen there is no change in colour, due to the direct action of light."

Bancroft[5] extended our knowledge of the action of light. "Light of every color from the extreme violet to extreme red and also ultra-violet and infra-red rays can cause chemical action. Those rays which act chemically on a substance must be absorbed by it, and the chemical action of light is closely connected with the optical absorption. Each color of the spectrum can have an oxidizing or reducing effect, depending on the nature of the light-sensitive substance. Dyes are oxidized most strongly by those rays which are absorbed. In all cases, however, the chemical action of light comes under the law that those rays are most effective which are absorbed by the light-sensitive substances. The most important oxidizing action of light is in the changing of organic materials and dyestuffs. We do not know whether the products obtained are the same as those resulting from electrolysis or not. We have a reducing agent, the organic substance, and an oxidizing agent, oxygen. Therefore, the conditions are favorable for decomposition by light."

[1] Wender: J. Chem. Soc., **66** II, 122 (1894).
[2] Z. physik. Chem., **79**, 639 (1912).
[3] J. Soc. Dyers Colourists, **18**, 206 (1902).
[4] Dreaper: "The Chemistry and Physics of Dyeing," 281 (1906).
[5] J. Phys. Chem., **12**, 209 (1908).

Other work extended this a little further in the actual oxidation process. Schaum[1] has stated that the oxidation process is affected by impurities. H, Cl, Br and SO_4 ions retard the action in the cases of inorganic substances; OH, NO_2 and ClO_4 ions accelerate it.

"Dyestuffs[2] which contain characteristic 'accelerating' groups, OH and NH_2, in the molecule are fugitive to light, while those containing groupings (H, SO_4, Cl and Br) recognized as possessing 'retarding' properties are little affected by exposure. Dyestuffs which from the presence of accelerating groups in the molecule are fugitive, become faster by the introduction of re-tarding groups and vice-versa. The action of light consists in bringing about a change in the 'dissociation conditions' or in the loosening of certain valences. The light rays bring the substance into a more reactive condition, producing a system which contains unsaturated active portions with free valences. In the destruction of colour by oxidation we have to deal with two chief processes:—

(1) Interaction between semi-dissociated oxygen molecules and the ions of water.

(2) The interaction between perhydroxyl ions and the colour.

"In the former, the reaction must be so influenced that the equilibrium resulting shall be favorable to the existence of perhydroxyl ions. In the latter, the peroxide formation must be retarded by the use of suitable catalysers or the perhydroxyl ions destroyed by means of suitable additions."

The same author[3] notes that a change of color may result from:—

(1) A molecular change in structure, (2) A change in the dissociation relations, (3) Oxidation and (4) Decomposition products.

It is surprising then to find two years later that he considers[4] that the fading of dyes on the fabric or in solution when exposed to light is an oxida-tion process, as no fading could be noticed in the experiments where oxygen was carefully excluded. Also Dreaper[5] says: "In the absence of oxygen there is no change in colour due to the direct action of light." Ellis and Wells[6] make the statement that basic colors do not fade in absence of air, although Dufton[7] says, "light is the most important factor, for it will decompose some colours in the absence of air and moisture."

It seems possible then that a rearrangement of the molecules or a molecular change in structure has been overlooked.

Work done in the Cornell Laboratory by Miss C. Gallagher[3] shows that some basic and acid colors may fade in the absence of oxygen.

[1] Eder's Jahrbuch, 1909, 120.

[2] K. Gebhard: J. Soc. Dyers Colourists, 25, 276, 304 (1909).

[3] K. Gebhard: Z. angew. Chem., 22, 1890 (1909).

[4] Gebhard: Färber-Ztg., 21, 253 (1911).

[5] "The Chemistry and Physics of Dyeing," 281 (1906).

[6] "The Chemical Action of Ultraviolet Rays," 315 (1925).

[7] J. Soc. Dyers Colourists, 10, 90 (1894).

[8] C. Gallagher: J. Phys. Chem., 36, 154 (1932).

Experimental

50 cc of a 0.01 g/liter solution of methyl violet, a basic dye was placed in an absorption bottle, equipped with two stop-cocks. Through this solution nitrogen was passed until it had displaced all the air. This was determined by means of a colorless solution of cuprous tetramminosulphate prepared by treating a solution of cupric sulphate with an excess of aqueous ammonia in the presence of copper gauze. Any air or oxygen present changes the colorless solution to the blue cupric tetramminosulphate.

The presence of oxygen could also have been detected by ammoniacal cuprous chloride, for Mitchell[1] explains that oxygen was determined by ammoniacal cuprous chloride. The gas was bubbled through the cuprous chloride in a modified Duboscq colorimeter. 0.01 cc of oxygen was detectable and further oxygen increased the depth of color in a linear relation.

One might object that even though the air was out, the water might furnish sufficient oxygen, but Ellis and Wells[2] report that water is not activated on exposure to ultraviolet light.

Two flasks containing the same amount of dye solution (methyl violet) were exposed to the light of the Fade-ometer. The first which contained air was faded colorless in 35 hours, and the second from which air had been displaced by nitrogen faded colorless in 28 hours. This indicates that some basic dyes will fade in the absence of air or oxygen. Although not proven, this is probably due to a rearrangement of the molecules due to the absorption of light which results in a chemical action.

Another basic dye, methylene blue, was exposed in the same manner. The sample which contained air was faded nearly colorless after 60 hours of exposure. The same amount in the flask filled with nitrogen faded to a lighter color in the same period of time. Thus basic dyes may fade in the absence of air or oxygen. It may be that half the dye was bleached by oxidation at the expense of the other half which was bleached by reduction.

In like manner, acid green and alkali blue, both acid dyes, were exposed in the Fade-ometer. After 60 hours, it was found that both dyes were bleached more in the flasks containing nitrogen than in those with air present. Apparently, some acid dyes may fade in the absence of air or oxygen also.

This is in line with the view expressed by Bancroft.[3] "What change takes place in any dye when exposed to light will depend on the chemical characteristics of the dye and on the chemical conditions prevailing when the dye is exposed to light."

"Only those rays[4] which are absorbed produce chemical action. The formulation of the chemical action of light is that all radiations which are absorbed by a substance tend to eliminate that substance. It is a question of chemistry whether any reaction takes place and what the reaction products are. Different radiations may cause the same substance to react in different ways."

[1] "Recent Advances in Analytical Chemistry," 1, 374 (1930).
[2] "The Chemical Action of Ultraviolet Rays," 311 (1925).
[3] J. Phys. Chem., 16, 529 (1912).
[4] Bancroft: Orig. Com. 8th Intern. Congr. Appl. Chem., 35, 59 (1912).

Also along the same line, Plotnikow[1] notes that all light which is absorbed tends to produce decomposition, but that not all rays are equally effective.

The Fading of Indigo on Wool and Cotton

"Indigo[2] is faster on wool than on cotton." This statement might possibly be explained on the basis that there is more of the reducing agent (sodium hydrosulphite) adsorbed on the wool than on the cotton, which would make the former faster. Bancroft[3] says: "The presence of a reducing agent should make oxidizable dyes more stable, at any rate until the reducing agent itself is oxidized. The alleged beneficial action of the sodium hydrosulphite with some colors is probably due to its being a reducing agent."

We were then interested in the relative adsorption of sodium hydrosulphite by wool and cotton. The gram samples of cotton and wool were placed in a closed flask containing the hydrosulphite solution for one-half hour. Then they were removed and the sodium hydrosulphite quickly titrated by the following method.[4] "An indigo solution is prepared by dissolving 2 grams of indigotin in sulphuric acid and diluting to one liter. 250 cc of this solution are poured into a flask of about 500 cc capacity, and whilst giving the flask a constant swirling motion, the hydrosulphite solution is carefully run in from a pipette until the blue colour changes to a pale yellow. The number of cc required multiplied by 2 gives the volume of hydrosulphite necessary to reduce 1 gm of indigotin."

This experiment showed that the wool adsorbed more of the sodium hydrosulphite than the cotton. Therefore, it would take longer to oxidize the sodium hydrosulphite adsorbed on the wool than on the cotton. Hence, in connection with the indigo, dyed cotton would fade faster than the wool. This is more theoretical than practical, and it can not be the entire answer to the problem. It does not account for the relatively large difference in fading time, and furthermore it would take only a short time to oxidize the adsorbed hydrosulphite.

If we neglect then the influence of the reducing agent, the problem divides itself into two parts. First, the samples of wool and cotton, which are the same weight, dyed in baths of equal concentration will adsorb indigo, and the one containing the greatest amount of dye will take longer to fade, because there is more dye on the cloth to bleach.

Secondly, if the two cloths contain the same amount of indigo and as far as possible with no excess sodium hydrosulphite on either, one might think that they would fade in the same time. Experiments reported later will show that this is untrue, for the rate of fading is different for the dyed cotton and wool.

Adsorption runs must be made to determine the rate of fading and also to show that one cloth takes up more indigo than the other from baths of

[1] Z. physik. Chem., **120**, 69 (1926).
[2] Stobbe: Z. Elektrochemie, **14**, 480 (1908).
[3] J. Phys. Chem., **19**, 145 (1915).
[4] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," **2**, 785 (1901).

equal concentration. The indigo used in these experiments was made available through the courtesy of the E. I. DuPont de Nemours Company.

The samples of wool and cotton were soaked in water for five days, then removed and allowed to dry for 24 hours in an oven at 50° C. Samples weighing one gram were used in the work.

Preparation of the Indigo Vat.

The manner of preparing the vat was obtained from Knecht.[1] In addition to giving directions he makes the following statement. "The hydrosulphite vats for dyeing wool may be prepared either with soda or lime in the same way as the hydrosulphite vats for cotton."

A solution of reduced indigo was prepared by placing 3 g of a 20% Du Pont indigo paste in a flask connected to a condenser, and to this was added 800 cc of hot water, 15 g of sodium hydrosulphite dissolved in water and diluted to 150 cc, and 50 cc of 0.12 N sodium hydroxide. The solution was heated for one hour at 80° C. The indigo was reduced to the light yellow leuco form.

The baths were prepared as outlined in the following tables and used to dye the 1 g samples of wool and cotton. The cloths were immersed for one hour, removed, squeezed dry and allowed to oxidize to the blue color in air. To determine the amount of indigo adsorbed on the fiber the amount left in solution was determined and subtracted from the original amount.

Method of Analysis.

This was obtained from Knecht.[2] The remaining solution of indigo was boiled for five minutes to be rid of the excess SO_2 and air was passed through to oxidize to the blue form, which precipitated in fifteen minutes. The solution was filtered through a Gooch crucible and the asbestos pad containing the indigo was placed in a 100 cc beaker. 5 cc of concentrated sulphuric acid was added and the contents heated to 40° C for one-half hour. This sulphonates the indigo to indigo carmine. This was diluted to 200 cc and a 50 cc portion taken for titration by titanous chloride to determine the amount of indigo.

0.35 g of Mohr's salt was dissolved in 100 cc of water and titrated with $TiCl_3$. According to Knecht this quantity is equivalent to 0.05 g of indigo. 0.35 g Mohr's salt required 112 cc $TiCl_3$.

$$\frac{0.05}{112} = 0.000446 \text{ g Indigo is equivalent to 1 cc } TiCl_3.$$

Titration of 50 cc of Standard dye solution.

The standard is taken as 30 cc reduced indigo and 20 cc water.

$$0.000446 \times \text{cc } TiCl_3 = \text{gm Indigo/50 cc.}$$

Run 1 $0.000446 \times 39.6 = 0.0177$ gm Indigo/50 cc.

Run 2 $0.000446 \times 39.8 = 0.0178$ gm Indigo/50 cc.

The average for the two runs is 0.01775 gms.

$$0.01775/50 = 0.000355 \text{ gms Indigo per cc.}$$

[1] "A Manual of Dyeing," **1**, 325 (1910).
[2] "A Manual of Dyeing," **2**, 822 (1910).

<div align="center">

TABLE I

The Adsorption of Indigo by Wool

</div>

Run	cc. reduced Indigo	cc. HOH	Orig. Conc. of bath	Final Conc. of bath	Adsorption
1	5	20	0.002958 g	0.000378 g	0.00258 g
2	10	15	0.005916	0.000856	0.00506
3	15	10	0.008875	0.001565	0.00731
4	20	5	0.011832	0.002332	0.00950
5	25	0	0.01479	0.00399	0.01080
6	30	0	0.017748	0.006368	0.01138

<div align="center">

TABLE II

The Adsorption of Indigo by Cotton

</div>

Run	cc. reduced Indigo	cc. HOH	Orig. Conc. of bath	Final Conc. of bath	Adsorption
1	5	20	0.002958 g	0.001208 g	0.00175 g
2	10	15	0.005916	0.003116	0.00280
3	15	10	0.008875	0.0041482	0.0047268
4	20	5	0.011832	0.005882	0.00595
5	25	0	0.01479	0.00827	0.00652
6	30	0	0.017748	0.010898	0.00685

Sample Calculations.

Using the data for run 3 in the adsorption of indigo by wool. After the wool was removed from the indigo bath, the latter was converted into indigo carmine as shown above. The solution was diluted to 200 cc and a 50 cc portion of this was taken for titration.

Run (a) 0.000446 $\times$ 0.9 cc TiCl$_3$ = 0.0004014 g in 50 cc.

0.0004014 $\times$ 4 = 0.0016056 g Indigo left in the bath.

Run (b) 0.000446 $\times$ 0.85 cc TiCl$_3$ $\times$ 0.0003791 g in 50 cc.

0.0003791 $\times$ 4 = 0.0015164 g Indigo left in the bath.

	Run 1	Run 2
Total indigo in 25 cc	0.008875 g	0.008875 g
Indigo left in the bath	0.0016056	0.0015164
Adsorbed indigo on 1 g wool	0.0072694	0.0073586

<div align="center">Average = 0.007314 g adsorbed</div>

The adsorption by cotton was carried out in the same manner as the wool. When the cotton was removed from the indigo bath, the latter was converted ·into indigo carmine. The solution was diluted to 200 cc and a 50 cc portion was taken for titration. The calculation for run 3 of the cotton adsorption follows:

Run (a) 0.000446 $\times$ 2.3 cc TiCl$_3$ = 0.001026 g in 50 cc.

0.001026 $\times$ 4 = 0.004104 g Indigo left in the bath.

Run (b) 0.000446 $\times$ 2.35 cc TiCl$_3$ = 0.0010481 g Indigo in 50 cc.

0.0010481 $\times$ 4 = 0.0041924 g Indigo left in bath.

	Run 1	Run 2
Total indigo in 25 cc	0.008875 g	0.008875 g
Indigo left in the bath	0.004104	0.0041924
Adsorbed indigo on 1 g cotton	0.004771	0.0046826

Average = 0.0047268 g adsorbed

The data in Tables I and II are plotted, and from the curves (Fig. 1) it is evident that there are differences in adsorptive capacity for the wool and
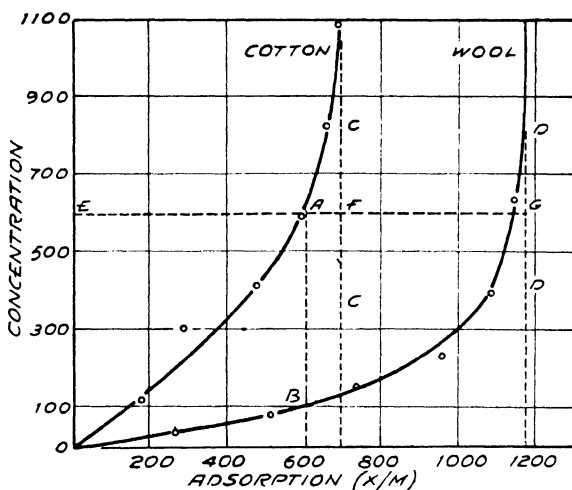
FIG. 1
Adsorption of Indigo by Wool and Cotton

cotton. From baths of equal concentration the sample containing the most dye will take longer to fade, because there is more indigo on the cloth.

Do the experimental facts confirm this? The dyed wool containing 0.00731 g of indigo (Run 3, Table I) was exposed simultaneously with the dyed cotton containing 0.0047268 g of indigo (Run 3, Table II). These two runs were made from 15 cc of reduced indigo and 10 cc of water, or the baths contained the same amount of indigo before adsorption.

The cotton sample faded completely in 158 hours of exposure to the carbon arc light, and the wool sample required 400 hours to bleach. Thus, the sample containing the greatest amount of indigo takes longer to fade. This is similar to the work done in this laboratory by Verbyla[1] on the fading of indigo-dyed cotton in which he showed that the larger the amount of indigo adsorbed on the cotton per unit area, the longer the time necessary in exposure to the Fade-ometer to effect fading.

Suppose that the two cloths contained the same amount of dye and as far as possible with no excess sodium hydrosulphite on either. Which would fade in the least time?

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[1] Verbyla: Unpublished Senior Research (1922).

From the adsorption curves we were able to calculate values which would give the same adsorption on the cotton and wool. Samples were prepared and analyzed and found to fall approximately on the 0.00600 g line.

	Cotton	Wool
	Cotton	Wool
Grams of dye in solution	0.011832 g	0.0070992 g
Grams of dye left in the bath	0.0058872	0.0010704
Grams dye adsorbed	0.0059448	0.0060288

This shows that the gram samples of cotton and wool contained nearly the same amount of adsorbed indigo.

The dyed wool and cotton were then exposed to the Fade-ometer, and the cotton faded completely in 198 hours of exposure, while the wool faded about 3/4 in 250 hours.

Since the gram samples of cloth contained approximately the same amount of dye, but faded in different times, the rate of fading must be the important factor. This can be best explained by means of the chemical potential.

Chemical Potential.

"Since reaction velocity[1] is probably directly proportional to the difference of chemical potential and inversely proportional to the chemical resistance, we can increase the reaction velocity either by increasing the difference of chemical potential or by decreasing the chemical resistance." Miller[2] showed that any material which increased the chemical potential of a toxic substance would likewise increase its toxicity.

In regard to chemical potential, we know that as we add a solute to a solution, it increases the chemical potential of the solute in the solution. In consequence of this we increase the rate at which the solute will react. The chemical potential then increases as we add solute until we reach saturation at which point the chemical potential of the solute in the solution is equal to that of the solid solute, which is a maximum value.

Dyeing is not necessarily the same case as a solute in solution, but there are similar considerations, for we increase the amount of dye on the cloth up to complete saturation of the cloth. The chemical potential of the dye on such a saturated cloth is at its maximum possible value. The nearly vertical portions of the adsorption curve is an adsorption value, which is but negligently increased even if the concentration of the dye in the solution goes up to a saturated solution. Just as the chemical potential of the solute in solution is proportional to the fractional saturation of that solution, so also any intermediate step on the adsorption curve is equivalent to a fractional saturation, which is in turn equal to the same fraction of the chemical potential of the solid dye.

Now, at any value of X/M, where X is the weight of indigo adsorbed, and M is the weight of the cloth, the degree of saturation, which is a function

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[1] Bancroft: "Applied Colloid Chemistry," 45 (1926).
[2] J. Phys. Chem., **24**, 562 (1920).

of the chemical potential is equal to $\dfrac{X/M}{X'/M} = k\ P$, where X'/M is the amount adsorbed at saturation, or on the flat part of the curve and P is the chemical potential. But M is the same value, i.e. one gram of cloth was used in all cases. Therefore, $k\ P = X/X'$. Then regardless of the relative position of the curves below saturation, the rate of bleaching of the two cloths containing the same amount of adsorbed dye is a function of P, or the bleaching is a function of the fraction expressing the degree of saturation at the concentration of the dye in the cloth. The more nearly saturated cloth will fade the faster.

The 0.00600 g line (A-B) in Fig. 1 represents the equal adsorption of indigo by one gram of cotton and one gram of wool and cuts the adsorption curve for cotton at A, and the adsorption curve for wool at B. C-C represents the maximum adsorption for the cotton, and D-D for the wool. Now the chemical potential may be expressed graphically for cotton as E A/E F and for wool as E A/E G.

Evaluating these expressions we have:

$$E\ A/E\ F = 0.00600/0.00690 = 0.87 = k\ P \text{ for cotton.}$$
$$E\ A/E\ G = 0.00600/0.01160 = 0.517 = k\ P \text{ for wool.}$$

Since the amount of dye on each cloth is the same the difference in fading must be due as shown to the greater chemical potential of the indigo on the cotton.

Conclusion.

We may say then that the reason indigo dyed on cotton fades faster than on wool is because its chemical potential is greater on cotton than on wool.

From baths of equal concentration the wool adsorbs more indigo than the cotton and will take longer to bleach, because there is more dye per unit weight of the fiber to fade. Under these conditions the influence of the rate of fading will be small in comparison with the case of equal adsorption of the dye by wool and cotton.

The Factors that influence Fading.

The fastness properties of dyestuffs have been treated by Heuthwaite.[1] "Photochemical reactions, which we will assume to be the main reactions in fading are reactions which are either initiated or accelerated by radiant energy (light), having a wave-length corresponding to those embraced by the visible spectrum and the ultraviolet region of the spectrum. The effect of the infra-red is usually regarded as due to heat rather than to light.[*] In nearly all the cases of photochemical effect the rate of reaction is proportional to the intensity of the light. Light may act as a catalyser in producing photochemical reactions, in which case the light accelerates (positively or negatively) a reaction which would of itself proceed in the dark or it may act as

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[1] Textile Colorist, **50**, 311 (1928).

[*] This cannot be true if the fading is done at a constant temperature. The light which is absorbed produces the change.

the originator of a reaction which would not go in the dark, or it may alter the course of a reaction so that different end products are obtained. In a general way we may say that photochemical reactions involve selective adsorption."

Many authors have suggested the factors that influence the fading of color. Thus Dreaper[1] claims that it depends on the character of the light, temperature, nature of the solvent, fiber and constitution of the dye. Rose[2] adds to these the intensity of the dyeing (shown with the work on indigo), quality of the substrate, and humidity. Most of these will be discussed later.

Finally, Appel[3] contributes to the long list including (1) atmospheric humidity, (2) other atmospheric influences—acid or alkaline vapors, (3) temperature—may have an effect, but probably not large, (4) spectral distribution of the radiation, for only radiations which are adsorbed can produce fading (the first law of Grotthuss) and dyeings show selective absorption, (5) intensity of the radiation, and (6) the visible and long wave-length ultraviolet radiation in sunlight are relatively more important in comparison with the short wave-length ultraviolet than is supposed.

In the same year, Anderson[4] says: "The tendency to fade and the acceleration of fading increases usually as the wave-length of the ultraviolet becomes shorter, for the shorter wave-lengths of the ultraviolet exert a much more powerful chemical action than the longer ultraviolet and visible radiation."

These many factors naturally led to the proposal of some chemical reaction which would simulate the conditions of fading. Grant and Elsenbast[5] worked out a method[6] for the rapid testing of dyes and pigments. They found that methylene blue, methyl violet, victoria green, magenta, azo red and eosine are bleached at ordinary temperatures by a suitable concentration of hydrogen peroxide. Similar bleaching effects were obtained with per-sulphate solutions. Unfortunately, when exposed to sunlight and in the light of the quartz mercury vapor lamp, the order of stability was not the same as in the oxidizing solutions. The discrepancy was due in part to the fact that oxidation of the dyes is not always due to light of the same wave-length.

Gebhard[7] objected to this method on the gounds that oxidations in the light may be wholly different from those in the dark, even when the same oxidizing agent is used. In the dark, the atomic oxygen from the oxidizing agent is the important factor, which is not so in the light. The real criticism was that the light of different wave-lengths may cause the oxidation to proceed in different ways.

[1] "The Chemistry and Physics of Dyeing," 281 (1906).
[2] Am. Dyestuff Reporter, **20**, 775 (1928).
[3] Am. Dyestuff Reporter, **20**, 755 (1928).
[4] Am. Dyestuff Reporter, **20**, 753 (1928).
[5] J. Phys. Chem., **16**, 546 (1912).
[6] Reported by Bancroft: Orig. Com. 8th Intern. Congr. Appl. Chem., **20**, 91 (1912).
[7] Z. angew. Chem., **26**, 79 (1913).

Then Holmes[1] showed that in the presence of uranium salts oxalic acid is decomposed by light, the reaction serving as an effective chemical photometer. The reaction is quantitative, and he suggested that it might be used in connection with the determination of the light-fastness of dyes.

Stern[2] thinks that some form of chemical energy may be found which imitates sunlight and is speedier. He suggests the use of polarized light.

None of these methods has been developed to any extent, and investigators have had to fall back on the artificial light source.

Discussion of Light Sources.

Since we must use some artificial light source for the following experiments on dyes and lakes, it will not be amiss at this point to discuss the various instruments. Gordon[3] compared the action of sunlight, mercury arc light (in quartz) and carbon arc light on a series of dyed samples representing various classes of dyestuffs. The two kinds of sunlight (New Jersey and Arizona) and the violet carbon arc showed much the same action in all cases, and it is his opinion that it would be best to make all tests of fastness either with sunlight or violet carbon arc light, preferably the latter. He showed that the carbon arc was more uniform throughout long periods than the mercury arc, which loses efficiency rapidly when in use, although Anderson[4] claims that there exists no artificial source of light, which resembles sunlight, and, with the exception of the quartz mercury arc, exceed the sun in the quantity of heat rays (infra-red) radiated.

"The character[5] of the spectral distribution of the fading source determines the character of the result, and where the source is equivalent to daylight, the fading results are comparable in color character. Fading is not caused by any one region, but is the result of the combination of certain regions and certain relative powers in each region."

"The ultraviolet radiation[6] without any of the visible spectrum being present produces fading, the amount of which depends on the quantity of radiation and the extent of the spectrum used. Visible radiations with no ultraviolet causes fading, and there is evidence that the infra red alone also has a fading action."

According to Toch[7] the decomposition of lake colors in sunlight is due entirely to the action of the rays of light from green to violet and the direct action of ultraviolet light.

"The mercury arc[8] should not be used for dye testing as some of the injurious wave-lengths are not present in the mercury spectrum."

[1] Am. Dyestuff Reporter, **13**, 188 (1924).
[2] J. Oil and Colour Chem. Assoc., **13**, 185 (1930).
[3] Textile Colorist, **43**, 29 (1921).
[4] Am. Dyestuff Reporter, **20**, 753 (1928).
[5] Busby: Textile Colorist, **45**, 151 (1923).
[6] Hedges: J. Soc. Dyers Colourists, **44**, 341 (1928).
[7] "The Chemistry and Technology of Paints," 299 (1925).
[8] Cunliffe: J. Text. Inst., **15**, 173 (1924).

The artificial source of light which seems the best when all factors are considered is the commercially available instrument known as the "Fadeometer," which contains a glass-enclosed carbon arc and means for holding the samples undergoing exposure at a definite distance from the light source. It was used by Reed and Appel[1] at the U. S. Bureau of Standards for work on the light-fastness of lithographic ink pigments. The carbon arc appears to be a reasonably satisfactory source of light for fading tests of lithographic inks. The light produced is rich in the longer ultraviolet and shorter visible wave-lengths. Its spectral distribution (the relative amounts of radiant energy of individual wave-lengths in proportion to the total energy) in comparison with sunlight is given in Table II.

TABLE II

Spectral distribution of the radiation* from the glass-enclosed arc lamp compared with sunlight at Washington, D. C., on
May 25, 1926, 11 to 12 a.m.

Spectral Range		Percent of the Total Radiation	
		Arc	Sun
170–320	mμ***	0.0	2.0
320–360	mμ	2.0	2.8
360–480	mμ	18.5	12.6
480–600	mμ	9.3	21.9
600–1400	mμ	16.5	38.9
1400–4200	mμ	22.1	21.4
4200–12000	mμ	31.6	0.4

*Measurements by W. W. Coblentz, Bureau of Standards.
**$I\mu$ = 0.001 millimeter = 1 micron. Visible light comprises wave-lengths between 400 and 700 mμ.

The glass-enclosed carbon arc gives little or no radiation below a wave-length of 320 mμ but much from 350 to 480 mμ."

A Corex glass globe was used to surround the carbon arc for it has been shown[2] that Corex glass transmits visible and ultraviolet light to beyond the limit of the ultraviolet in sunlight.

Coblentz and Stair[3] give data on the decrease in transmission of Corex glass which occurs after exposure to the carbon arc. The Corex Glass transmission is 60–65%, which is based on the transmission properties at 302 mμ after solarization (the photo-chemical reaction most of the glasses undergo on exposure to sunlight—usually loss of transparency). The Corex glasses have a sharp cut-off at 290 mμ.

The Effect of Humidity.

The humidity has an influence on the amount of fading, for of two samples[4] of material exposed to the light, one of which is placed in moist, the other in dry air, the former will lose its color far more quickly than the latter.

[1] J. Research U. S. Bureau Standards, **3**, 359 (1929).
[2] Appel and Smith: Am. Dyestuff Reporter, **17**, 410 (1928).
[3] J. Research U. S. Bureau Standards, **3**, 629 (1929).
[4] Joffre: Bull., **49**, 860 (1888).

Gebhard[1] showed that moisture accelerates the fading, and he is supported by Cunliffe[2] who pointed out that increased humidity generally caused more rapid fading of dyed fabrics exposed to the light.

Since the Fade-ometer in the laboratory was of the old type not containing an electric ventilator and humidifier, the moisture was supplied by water contained in vessels placed on the base plate. These were kept full at all times. In order to eliminate the possible influence of any generated heat and ozone, two large electric fans were directed at the glass-enclosed carbon arc in such a manner as to drive the heat or ozone out of the top of the cabinet. Columbia violet carbons were used to form the arc.

Investigations on the Fading of Dyes on Wool, Silk and Cotton.

Many experiments[3] were done on the fastness of sixty-three different dyes on wool and cotton. An arbitrary classification of the fastness was developed for them, and the conclusions that the author draws are as follows:

"In this study it has been shown that a photometer can be used with satisfactory results in testing the fastness of dyes, and that the measurement of only one primary color is necessary for the test. It has also been shown that increasing the concentration of a dye fourfold increases its fastness probably about 60%."

Cady and Appel[4] worked with 1,252 specially prepared dyeings on cotton, wool, silk and weighted silk. They were exposed to daylight in several different ways and to the light from a glass-enclosed carbon arc. 381 different coloring matters were used. Details were given concerning the samples used, the method of exposure, the method of studying results and the results of exposure. They concluded that fading in the arc light is different in quality in many instances from that in the "standard sun test," which they formulated.

The Fastness of Lithographic Ink Pigments to Light

At the same time, the light-fastness of lithographic ink pigments was tested. "The yellowing[5] of the varnish in the absence of light and its bleaching in strong light must be taken into consideration in judging the fastness of pale colors. The heat during the exposure affects certain prints and causes a reversible change in color. Since the fastness of a given pigment depends on its concentration in the ink film of the print, each pigment may be given more than one fastness classification according to its concentration."

■ However, our experiments are not so much concerned with giving a fastness classification to dyes as with learning more about fading.

In the literature we find the statement[6] that lakes are less sensitive to light than the free colors. Grant and Elsenbast[7] studied the action of hydro-

[1] Färber-Ztg., **21**, 253 (1911).
[2] J. Soc. Dyers Colourists, **45**, 215 (1929).
[3] Gordon: Textile Colorist, **43**, 29 (1921).
[4] Am. Dyestuff Reporter, **18**, 407 (1929).
[5] Reed and Appel: J. Research U. S. Bureau Standards, **3**, 359 (1929).
[6] Eder: Handbuch der Photographie, **2**, 384 (1910).
[7] J. Phys. Chem., **16**, 546 (1912).

gen peroxide and sunlight on the following lake colors: eosine, vermilion, scarlet lake, Ian red, red lake, eosine lake, magenta lake, blue mauve, green lake deep, and green lake yellowish. They were more stable to hydrogen peroxide and sunlight than the corresponding dyes.

Since we wished to compare the action of the carbon arc light on dyes and lakes, the acid dyes were exposed with their corresponding aluminum lakes. Also the basic dyes were compared with the tannin lakes of the same dyes.

Preparation of Alumina.

1200 cc of a 10% solution of aluminum sulphate equivalent to 120 g is mixed with 500 cc of a 10% solution of soda. The aluminum sulphate solution is heated to 60° C and the soda ash solution added at 80° C rapidly with stirring. The alumina was washed five times and a white colloidal solution was obtained.

In order to obtain the amount of Al_2O_3 present 50 cc were evaporated to dryness and weighed.

Results:—Run 1 = 0.4085 g in 50 cc
Run 2 = 0.4030 g in 50 cc
Run 3 = 0.4050 g in 50 cc
Average = 0.4055 g in 50 cc

For a purer alumina it is better to make it from aluminum chloride and ammonium hydroxide or by the preparation from sheet aluminum with the action of water after the aluminum has been activated.

Bancroft[1] states that in the sulphate method of making alumina, the sulphate coagulates the hydrolyzed salt so readily that large amounts of alumina or basic salt are precipitated in the bath or in the fiber in such a form that it readily rubs off.

However, the aluminum sulphate method was used in order to check some other results by Reed and Appel at the Bureau of Standards.

The acid dyes selected for use in these experiments were (1) acid green, (2) alkali blue and (3) azo-geranine, prepared by the British Dyestuffs, Ltd. The reason for selecting these is that they give different colors—(1) green, (2) blue and (3) red. Also the acid green and alkali blue are of the triphenyl-methane class, which would give a comparison between two dyes of the same chemical group, and azo-geranine is of the azo group which would allow a comparison between the dyes of two of the most important acid dyestuff groups.

The basic dyes were: (4) magenta and (5) methyl violet. These are both of the triphenylmethane class which would give a comparison between them and also with the acid dyes of the same group. All the acid dye solutions were prepared by dissolving 2 g in 500 cc of warm water and then diluting to one liter.

The lead acetate solution was prepared by dissolving 6 g in 500 cc of water.

"Acid dyes[2] are precipitated from solution by soluble salts (metallic) such as barium chloride, aluminum sulphate and lead acetate."

[1] J. Phys. Chem., **26**, 515 (1922).
[2] Heaton: "Outlines of Paint Technology," 183 (1928).

Acid Green Lake.

A simple lake may be prepared from alumina, acid green and lead acetate. The alumina adsorbs the dye and the lead acetate precipitates the color, which thus puts it in the insoluble form on the alumina.

The determination was first made on the precipitation of acid green by lead acetate, and it was found that 56 cc of the solution precipitated 28 cc of the acid green. This amount of dye was adsorbed by 60 cc of alumina, containing as previously indicated 0.4055 gms Al_2O_3 in 50 cc. The dye solution was prepared by diluting 28 cc of the acid green to a volume of 144 cc.

Glass flasks were made of one centimeter thickness with a capacity of 50–55 cc and so that a flat side would face the light. Into these were placed 50 cc of the dye solution and the same amount of lake. The latter has a tendency to settle, so a slow stream of air was passed through to keep it stirred. In order to have the dye under the same conditions it was treated similarly. The flasks were then exposed to the light of the Fade-ometer. The dye solution faded completely in 175 hours. This is not comparable to the results of the subsequent fading of prints, but it must be taken into account that the light has to pass through another layer of glass. A curious result was obtained with the lake. When exposed for eight hours, the green was stripped off the alumina, leaving the latter practically white; and the green agglomerated into very hard particles in the bottom of the flask. At the same time, the main body of the solution was colored violet. This may be due to a partial decomposition of the green color and the stripping of the alumina by the action of light. Since a current of air was passed through it may be a case of oxidation of the green and weakening of the forces of adsorption. However, air was also passed through the dye solution, but no such change as the violet color was noted. The lake was treated with 3% and 30% hydrogen peroxide in varying amounts, but no similar reaction was observed. Hence it is not solely an oxidation phenomenon. Then the dye was treated with sodium hydrosulphite, a reducing agent, to indicate whether some reduction had taken place. A yellow-green color resulted, but there was no appearance of the violet color as obtained in the fading of the lake. The lake was treated also but did not undergo the change which occurred when it was exposed to the carbon arc. Therefore, it does not look like a straight reduction.

The effect of increased temperature might cause it, and a sample was heated. The lake coagulated, but did not exhibit the violet color, and the dye does not change on heating.

Although not proved, the change is probably due to a partial decomposition of the dye under the influence of light in the presence of alumina as a catalytic agent.

Alkali Blue Lake.

An alumina lake of alkali blue was prepared by heating 40 cc of the dye for fifteen minutes, and then 25 cc of alumina was added. The dye was precipitated at 60° C with 0.08 g of aluminum sulphate (iron-free) in 5 cc

of water. The total volume was made to 70 cc. The dye solution was prepared by using 40 cc of alkali blue and 30 cc of water. They were exposed to the carbon arc light as indicated before.

The dye faded about 3/4 in 75 hours of exposure, while the lake faded only slightly in the same period. The exposure was continued until 164 hours had passed but only an additional slight fading was noted. Therefore, we may say that the alumina lake of alkali blue is more stable than the dye. This is due to the adsorption of the dye on the alumina, which fixes it so that there is less chance for a chemical reaction to take place due to the absorption of light.

One cc of the dye was treated with 50 cc of 3% hydrogen peroxide and the color was bleached somewhat in 80 hours, but not as much as that exposed in the Fade-ometer. The blue color decreased in color intensity and some particles of solid matter settled out, which was not so with the exposed sample. Another sample was treated with superoxol and no further effect was noted. Therefore, the hydrogen peroxide does not fade the color as much as the carbon arc lamp, because the activation of the dye by the light is important to produce fading. Hydrogen peroxide is a stronger oxidizing agent than air, and we should expect it to bleach the dye faster than in the air provided the dye was activated by light in both cases.

The lake treated with the same amounts of hydrogen peroxide (3% and 30%) showed relatively little bleaching in the same period of time.

The color then is bleached less with the hydrogen peroxide than with artificial light.

Azo-geranine Lake.

An alumina lake was prepared by adding 15 cc of the dye solution to 25 cc of the alumina and then precipitating with 30 cc of lead acetate solution. The dye solution was prepared by using 15 cc of the azo-geranine and 55 cc of water. These were exposed to the light of the carbon arc as previously shown with acid green.

The dye faded nearly completely in 160 hours of exposure, while the lake was faded about one half. The exposure was continued until 161 hours had passed but not much further change could be noted. Therefore the alumina lake of azo-geranine is faster to the light than the dye. The dye is also faster than alkali blue, for the latter with a larger concentration faded in less time.

One cc of the dye was treated with 50 cc of 3% hydrogen peroxide and the color was faded about one half in 160 hours, but not as much as the exposed sample. A fresh sample was treated with superoxol. The color faded about as much as the one treated with 3% hydrogen peroxide.

Therefore, the hydrogen peroxide does not fade the color as much as the carbon arc lamp in the same period of time.

Methyl Violet Lake.

We were next interested in the exposure of basic lakes and the corresponding dyes. For the preparation of the lake, a commercial formula was used. 3 g of methyl violet were dissolved in 300 cc of hot water, 2 g of acetic acid

added, and then 5 g of tannic acid (mordant) dissolved in 100 cc of hot water, and 2.5 g of tartar emetic (fixing agent) in 50 cc of hot water were added at 90° C. A deep blue-violet lake resulted. The dye was prepared by dissolving 3 g of methyl violet in 300 cc of hot water, 2 g of acetic acid and then 150 cc of water.

50 cc samples of each were exposed to the light. The dye faded almost completely in 28 hours of exposure, while the lake darkened slightly (discussed later). The colors were compared with the original samples by colorimetric methods. The lakes were dried, rubbed out with varnish and compared on paper and only a slight darkening was noted. Hence, the tannin lake of methyl violet is faster than the corresponding dye.

One cc of the dye was treated with 50 cc of 3% hydrogen peroxide for 28 hours and the color was lighter than the standard. When a larger amount was added the solution became colorless. The lake was faded very slightly by the same treatment.

Therefore hydrogen peroxide will fade the methyl violet solution, which checks the work of Grant and Elsenbast,[1] but it is not as rapid in its action as the light.

Magenta Lake.

1 g of magenta was dissolved in 200 cc of hot water, 0.5 g of acetic acid added, and then 3 g of tannic acid (mordant) dissolved in 100 cc of water, and 1.2 g of tartar emetic (fixing agent) in 50 cc of water were added at 90° C. A deep red lake resulted. The dye was made by dissolving 1 g of magenta in 200 cc of hot water, 0.5 g of acetic acid added and then 150 cc of water.

50 cc samples of each were exposed to the light. 63 hours were required to fade the dye, but the lake darkened considerably going over to a red-blue shade in 102 hours of exposure. It was thought that this might be due to some heat effect, but no darkening was observed when the standard lake was heated at varying temperatures. The effect may be due to the air bubbling through the lake, but air passed through did not produce a darkening. Experiments showed also that it was not due to a simultaneous action of the two factors.

The next factor examined was the action of light on tannic acid, and it was found that it darkened considerably on 52 hours of exposure, which would account for the darkening of the lake. Thus, the tannin lake of magenta is more stable to light than the dye. Also the dye is faster than methyl violet, another member of the triphenylmethane class.

One cc of the dye was treated with 50 cc of 3% hydrogen peroxide for 10 hours and the color was destroyed. However, the lake was altered only slightly under this treatment. Thus hydrogen peroxide will fade the magenta solution and in faster time than it acted on methyl violet, although the fading by the light is the reverse.

[1] J. Phys. Chem., **16**, 546 (1912).

The Fastness of Lakes.

According to Bancroft[1] many dyes are faster to light in iron, copper and chromium mordants than in aluminum or tin mordants. It is probable, though not proved, that this is due to certain wave-lengths being absorbed more or less completely by the colored mordants.

Preparation of Mordants.

(a) Alumina—This has been described previously.

(b) Chromium—The method for the preparation of the chromium mordant was taken from the work of Knecht.[2]

40 g of chromium sulphate were dissolved in 750 cc of water at 70° C and precipitated with 30 cc of concentrated ammonium hydroxide. Washed four times, and a greenish-blue hydrous oxide was obtained. In order to determine the amount of Cr_2O_3 present 50 cc were evaporated to dryness and weighed.

$$\text{Results:—Run 1} = 1.08 \text{ g}$$
$$\text{Run 2} = 1.083 \text{ g}$$
$$\text{Run 3} = 1.103 \text{ g}$$
$$\text{Average} = 1.089 \text{ g } Cr_2O_3 \text{ in 50 cc}$$

(c) *Tin Mordant.* Knecht, Rawson and Loewenthal[3] suggest the use of stannic chloride in the preparation of this mordant.

40 g of stannic chloride were dissolved in 750 cc of water at 70° C and precipitated with 50 cc of concentrated ammonium hydroxide. The mordant was washed four times. It was then peptized by a small amount of hydrochloric acid, and a white hydrous oxide of tin was obtained. However, this did not stay in suspension but had a tendency to settle out. Before use it was thoroughly shaken to distribute the particles.

In order to determine the amount of the oxide present, 50 cc were evaporated to dryness and weighed.

$$\text{Results:—Run 1} = 0.3930 \text{ g}$$
$$\text{Run 2} = 0.3950 \text{ g}$$
$$\text{Run 3} = 0.4000 \text{ g}$$
$$\text{Average} = 0.3960 \text{ g tin oxide in 50 cc}$$

Zinc Mordant.

40 g of zinc chloride were dissolved in 750 cc of water at 70° C and precipitated with 25 cc of concentrated ammonium hydroxide. The mordant was washed four times, and hydrochloric acid was added to give it a positive charge, but it did not stay up in suspension.

To determine the amount of ZnO present, 50 cc of the mordant were evaporated to dryness and weighed.

$$\text{Results:—Run 1} = 0.9150 \text{ g}$$
$$\text{Run 2} = 0.9080 \text{ g}$$
$$\text{Run 3} = 0.9110 \text{ g}$$
$$\text{Average} = 0.9113 \text{ g ZnO in 50 cc}$$

[1] J. Phys. Chem., **19**, 145 (1915).

[2] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," **1**, 240 (1910).

[3] "A Manual of Dyeing," **1**, 271 (1910).

Iron Mordant.

40 g of ferric chloride were dissolved in 750 cc of water at 70° C and precipitated with 40 cc of concentrated ammonium hydroxide. The mordant was washed four times, and a reddish-brown hydrous oxide was obtained, which settled out after standing.

To determine the amount of Fe_2O_3 present, 50 cc were evaporated to dryness and weighed.

$$\text{Results:—Run 1} = 0.8130 \text{ g}$$
$$\text{Run 2} = 0.8130 \text{ g}$$
$$\text{Run 3} = 0.8085 \text{ g}$$
$$\text{Average} = 0.8115 \text{ g } Fe_2O_3 \text{ in 50 cc}$$

Copper Mordant.

40 g of $CuSO_4.5H_2O$ were dissolved in 750 cc of water at 70° C and precipitated with 14 cc of concentrated ammonium hydroxide. The mordant was washed four times, and a blue-green hydrous oxide was obtained, which settled out almost immediately on standing.

To determine the amount of the oxide present, 50 cc were evaporated to dryness and weighed.

$$\text{Results:—Run 1} = 2.3220 \text{ g}$$
$$\text{Run 2} = 2.4350 \text{ g}$$
$$\text{Run 3} = 2.3860 \text{ g}$$
$$\text{Average} = 2.3810 \text{ g of the oxide in 50 cc}$$

Preparation of the Acid Green Lakes.

(a) *Alumina Lake*—This has been described previously.

(b) *Chromium Lake*—To 24 cc of the chromium mordant, equivalent in terms of the oxide to 60 cc of alumina, were added 28 cc of Acid Green G. This was precipitated with 56 cc of lead acetate solution.

(c) *Tin Lake*—To 60 cc of the tin mordant, equivalent in terms of the oxide to 60 cc of the alumina, were added 25 cc of the dye, and precipitated with 56 cc of lead acetate solution.

(d) *Zinc Lake*—To 30 cc of the zinc mordant, equivalent in terms of the oxide to the weight of 60 cc of alumina, were added 28 cc of the dye, and this was precipitated with 56 cc of lead acetate solution.

(e) *Copper Lake*—To 11 cc of the copper mordant, equivalent in terms of the oxide to the weight of 60 cc of alumina, were added 28 cc of the dye, and this was precipitated with 56 cc of lead acetate solution.

(f) *Iron Lake*—This was prepared in the same manner as the other lakes, but the lake was not printed because the brown colored iron mordant in combination with the green color gave a poor color which was not at all comparable to the other lakes.

Preparation of Prints.

The prints for the acid green lakes and for all the following lakes were made in the same manner. The lakes were prepared so that they would settle out and could be filtered. The lake was dried and an ink was formed

by mixing 0.1 g of the lake with 7 drops of a litho varnish until a smooth consistent ink was formed. The ink was then printed by means of a hand brayer on a good grade of white paper, care being taken to obtain an even print. Since the amount of ink[1] on the paper will affect the results, five or six prints of the same lake were prepared, exposed and the results taken as an average of these prints. After a little practice it was found that the prints could be made nearly identical, for they have the same appearance and fade in precisely the same time. All the prints were exposed at an equal distance from the arc, and some were removed before complete fading in order to show the stages. Where possible the prints for a given lake were exposed all at the same time and complete fading was taken as the end point, for a measure of half fading, etc., is relative and depends to a large extent on the observer.

Results of the Fading of Acid Green Lakes.

<div align="center">TABLE III</div>

1. The aluminum lake fades completely in 9 hours.
2. The tin lake fades completely in 4 hours.
3. The zinc lake fades completely in 7 hours.
4. The chromium lake fades completely in 12 hours.
5. The copper lake fades completely in 15 hours.
6. The iron lake was not printed due to the poor color.

For this dye the aluminum, tin and zinc lakes fade faster than the chromium and copper lakes, which supports the statement that lakes on colored mordants are less sensitive to light than those on the colorless mordants.

This is probably due to the colors of the mordants. Since copper and chromium mordants are colored they will absorb some of the effective light and thus cut down the fading of the dye. If this is true, then an alumina or any other colorless mordant lake ought to be faster if all except the blue rays are cut off, which is really the case with these two colored mordants.

In line with this, Scheurer[2] found that many direct cotton colors as well as indigo on cotton are rendered faster to light treatment in boiling copper sulphate solution. This is due to a certain amount of the copper salt being fixed in the fiber, which does not allow the chemical rays to pass. Stobbe[3] noted that many colors were made more stable to light by the addition of copper sulphate, which was taken up by the fiber to form copper mordant. He attributed this effect to the fact that copper mordant cut off some of the rays which did the most damage.

Effect of Color Screens on Fading.

Since the colored mordants probably cut off some of the effective light rays, an alumina lake of acid green behind a blue color screen ought to be faded less than one exposed in the usual way or one exposed behind a red color screen.

[1] Reed and Appel: J. Research U. S. Bureau Standards, **3**, 359 (1929).
[2] J. Soc. Dyers Colourists, **5**, 44 (1889).
[3] Eder's Handbuch der Photographie, **1**, 389 (1906).

Three prints of the alumina-acid green lake were exposed to the light. In front of one was placed a blue glass, for the second a red glass, and for the third a colorless glass, all of the same thickness. Undoubtedly, the glass itself will cut off some rays by reflection and refraction so that the colorless glass was used to make the conditions as nearly alike as possible.

The sample exposed behind the red glass faded in 164 hours and behind the colorless glass in 162 hours; while the sample behind the blue glass resisted the action of light for 200 hours with only a small amount of fading. The blue glass is acting like the colored mordants and is cutting off the most effective rays. The red glass transmits the red rays and the color is faded in approximately the same time as the print behind the colorless glass. Thus the blue cuts off the damaging rays and acts like the copper and chromium mordants.

The results in Table III show us that the tin lake fades in less time than the zinc and the latter in less time than the alumina. Dreaper[1] says that it will be remembered that the fastness of lakes depends on the nature of the absorbing material."

"The fastness[2] of a mordant colour to light will depend to some extent on the mode of fixation but principally on the mordant employed. Thus, fustic dyed on wool on a tin mordant gives a yellow, which is not at all fast to light, but with a chromium mordant (Bichromate) the yellow obtained with the same colouring matter may be classified as fairly fast."

Since the colorless mordant lakes were prepared using the same amount of dye, the same quantity of mordant calculated on the basis of the anhydrous oxide and the same volume of lead acetate to precipitate the dye, the differences in fading time must be due to the rates of fading of the dye on the several mordants. Again, we must deal with the chemical potential of the dye on the various mordants.

The explanation for the faster fading of indigo adsorbed on cotton than when adsorbed on wool was based on the fact that the indigo adsorbed on the cotton was at a greater chemical potential. The theory has been outlined in that case, and we need not repeat it here for these are analogous cases, except that we are using a mordant in place of the fiber. In order to determine the chemical potentials of the dye on the mordants, adsorption experiments were run.

Adsorption Curves for Acid Green on Alumina, Tin and Zinc.

The determination for the adsorption curves were run by adding a known amount of dye to a fixed amount of mordant, analyzing the supernatant liquid for the unadsorbed dye and then calculating the amount adsorbed by the mordant.

For example in run 1, Table IV, to 10 cc of the alumina was added 60 cc of a dye solution, prepared from 1 cc of dye (2 g/liter) and 59 cc of water. The mordant and the dye were mixed well and allowed to come to equilibrium

[1] "The Chemistry and Physics of Dyeing," 281 (1906).

[2] Knecht, Rawson, and Loewenthal: "A Manual of Dyeing," 2, 746 (1910).

over night.   Then 5 cc of the supernatant liquid was used for a colorimetric determination in a Kober colorimeter against a standard containing the dye used in the preparation of the lake.   The colorimeter was adjusted for the zero point with a known standard.

Sample Calculation.

For example in run 3, the standard was set at 5 and to obtain a color match the unknown had to be set at 33.   In this run the dye used contained 0.03 g of acid green.

Then .03/x = 33/5.   x = 0.00455 g acid green left in solution.

Original conc. − conc. in solution = amount adsorbed
0.03 g − 0.00455 g   = 0.02545 g adsorbed by 10 cc of
alumina.

The values for the concentration and adsorption for acid green on alumina, tin and zinc mordants are given in Table IV.

TABLE IV

Acid green—Alumina

Run	Am't Dye	Am't Water	Orig. Conc.	Equil. Conc.	Adsorption
1	1 cc	59 cc	0.002 g	0 g	0.002 g
2	5	55	0.010	0.000587	0.009413
3	15	45	0.030	0.00455	0.02545
4	25	35	0.050	0.0117	0.0383
5	50	10	0.100	0.0432	0.0568
6	60	0	0.120	0.0606	0.0594

Acid green—Tin

| Run | Dye solution | | Orig. Conc. | Equil. Conc. | Adsorption |
	Am't Dye	Am't Water			
7	1 cc	59 cc	0.002 g	0 g	0.002 g
8	5	55	0.010	0.00275	0.00725
9	15	45	0.030	0.0107	0.0193
10	25	35	0.050	0.0230	0.0270
11	50	10	0.100	0.0607	0.0393
12	60	0	0.120	0.0802	0.0398

Acid green—Zinc

Run	Am't Dye	Am't Water	Orig. Conc.	Equil. Conc.	Adsorption
13	1 cc	59 cc	0.002 g	0.000987	0.001013
14	5	55	0.010	0.00376	0.00624
15	15	45	0.030	0.0121	0.0179
16	25	35	0.050	0.0205	0.0295
17	50	10	0.100	0.0532	0.0468
18	60	0	0.120	0.0710	0.0490

From the data given above curves (Fig. 2) were plotted for the adsorption of acid green by alumina, tin and zinc mordants.

The adsorption values for the lakes as originally prepared fall on the 0.0093 line (line B) of the curves. The maximum adsorption for tin is represented by line C, for zinc by line D and for alumina by E.

Now, at any value of X/M, where X is the weight of acid green adsorbed, and M is the weight of the mordant, the degree of saturation, which is a
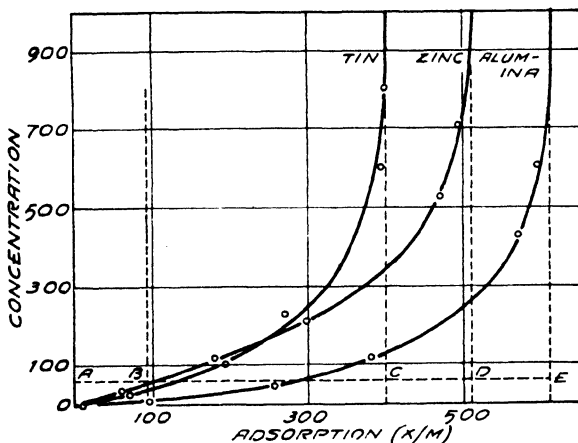
FIG. 2

Acid Green Adsorption Curves

function of the chemical potential is equal to $\dfrac{X/M}{X'/M} = k\,P$, where X'/M is the amount adsorbed by the mordant at saturation, or on the flat part of the curve, and P is the chemical potential. But M is the same value for the same amounts of mordant were used. Therefore, $k\,P = X/X'$. Then the rate of fading of the dye on the various mordants is a function of P, or the fading is proportional to the fraction expressing the degree of saturation at the concentration of the dye on the mordant. The dye on the more nearly saturated mordant will fade the faster.

The chemical potential may be expressed graphically for tin as AB/AC; for zinc as AB/AD and for alumina as AB/AE.

Evaluating these expressions we have:

Chemical Potential for dye on Sn = AB/AC = 93/400 = .2325
   ”   ”   for dye on Zn = AB/AD = 93/510 = .183
   ”   ”   for dye on Al = AB/AE = 93/610 = .1525

Then the acid green on the tin mordant should fade faster than on zinc, which should fade faster than on alumina, because the chemical potentials for the dye on the mordants are in that order.

The mordants used in the adsorption experiments were freshly prepared, but if one uses an aged alumina the conditions are entirely different. An alumina mordant which had aged for a month was used for lake formation

with acid green and the print prepared and exposed in the same manner as before. However, the print was faded in comparison with the tin-acid green lake in which the mordant was fresh. The alumina lake faded in less time than the tin lake, which must mean that the dye was at a higher chemical potential under these conditions than the dye on the tin mordant. The time for the alumina lake to fade was 3 hours, and for the tin 4 hours. Adsorption experiments were run with the aged alumina and the results plotted against the adsorption data for hydrous tin oxide. The data for the alumina adsorption are given in Table V.
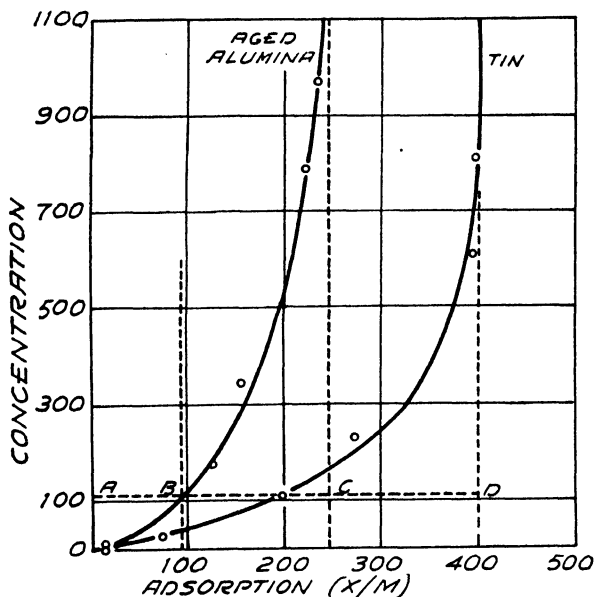
FIG. 3
Acid Green Adsorption Curves

TABLE V

Acid green—alumina (aged)

Run	Dye solution		Orig. Conc.	Equil. Conc.	Adsorption
	Am't Dye	Am't Water			
1	1 cc	59 cc	0.002 g	0.000967 g	0.001033 g
2	5	55	0.010	0.00462	0.00538
3	15	45	0.030	0.0176	0.0124
4	25	35	0.050	0.0345	0.0155
5	50	10	0.100	0.0780	0.0220
6	60	0	0.120	0.0964	0.0236

The curves (Fig. 3) were plotted using the data in Table V for alumina, and in Table IV for tin. We find that the adsorption curve for alumina has shifted. Consequently the chemical potential of the dye adsorbed must change. The chemical potentials as calculated from the curves are as follows:

For the dye on tin, $AB/AD = 93/400 = .2325$
For the dye on alumina, $AB/AC = 93/245 = .38$

Therefore, since the chemical potential for the dye on the alumina is higher in this case than on tin, we should expect it to fade more rapidly than on the tin mordant. This confirms the exposures.

Effect of Precipitating Agent on Fastness.

Bancroft[1] indicated that by changing the nature of the precipitating agent it ought to be possible to vary the fastness of the lakes to light.

A lake was prepared from acid green, alumina and lead acetate as shown previously; and another in the same manner but precipitated by barium chloride. Prints were made and exposed simultaneously to the carbon arc light. It was found that the lake precipitated with lead acetate faded in nine hours, while the one precipitated with barium chloride resisted the action of light for eleven hours. This must mean that there is a difference in the adsorption and that the dye precipitated with lead acetate is at a higher chemical potential that than precipitated with barium chloride. In other words the barium dye complex is adsorbed more than the lead dye complex.

Preparation of Azo-geranine Lakes.

(a) *Alumina Lake*—This has been shown before.

(b) *Chromium, Iron, Tin, Zinc and Copper Lakes*—These were all prepared by adding 45 cc of the azo-geranine solution to the mordant and precipitating with 90 cc of lead acetate solution. The amounts of mordants used were— 30 cc of chrome, 38 cc of iron, 75 cc of tin, 38 cc of zinc and 14 cc of copper— all equivalent as anhydrous oxides to the weight of 75 cc of alumina calculated as Al_2O_3.

Results of the Fading on Azo-geranine Lakes.

TABLE VI

1. The aluminum lake fades completely in 6 hours.
2. The tin lake fades completely in $4\frac{1}{2}$ hours.
3. The zinc lake fades completely in 3 hours.
4. The chromium lake fades completely in 8 hours.
5. The copper lake fades completely in 7 hours.
6. The iron lake changes color but does not fade completely in 17 hours.

In general, it would be foolish to employ colored mordants except iron to make red lakes, but this work was carried out using the colored mordants in order to show the results for the different dyes.

For this dye then the aluminum, tin and zinc lakes fade in less time than the chromium, iron and copper lakes, which again shows that the lakes on the colored mordants are less sensitive than those on the colorless.

[1] Orig. Com. 8th Intern. Congr. Appl. Chem., **20**, 59 (1912).

However, it is interesting to note in this case that the difference in fading time between the colored mordant and the colorless mordant lakes is far less than with the corresponding acid green lakes. This must mean that the colored mordants are less effective in absorbing the light rays which produce the fading.

Effect of Color Screens on Fading.

Three prints of the alumina-azo geranine lakes were exposed to the light—one behind the blue glass, another behind red, and the third behind the colorless glass. The sample behind the colorless glass faded almost entirely in 98 hours, while the sample behind the blue glass faded in 110 hours, and that behind the red in 156 hours. This shows that the blue glass in this case is far less effective in cutting off the damaging rays than with the acid green lake. On the other hand the red glass is much more effective. Table VII shows the difference between the two dyes.

TABLE VII

Alumina Lake		Glasses		
of	None	Colorless	Red	Blue
Acid Green	9 hrs.	162 hrs.	164 hrs.	200 hrs.*
Azo-geranine	6 hrs.	98 hrs.	156 hrs.	110 hrs.

*Small am't of fading.

There is a marked difference in fading time when the glasses are used. The acid green lake is faded more by the rays at the red end of the spectrum and the blue glass is effective in cutting most of the rays off. With azo-geranine the blue end of the spectrum is the more effective and thus the blue glass has much less absorbing power for the rays which cause the fading. The red glass cuts off the damaging rays and thus makes the color more stable in this case.

This accounts then for the difference in fading between the colorless and colored mordant lakes being greater in the case of acid green than in that of azo-geranine. For acid green the red rays are most effective and the blue mordants cut them off. With azo-geranine the blue rays are the most effective and the mordants do not cut them off.

With the colorless mordants, azo-geranine faded faster on zinc than on tin, which faded faster than the alumina lake. The chemical potential for the dye on the mordants must be different in this case than with the acid green lakes. In order to determine this, adsorption experiments were done.

Adsorption Experiments for Azo-geranine.

Adsorption runs for azo-geranine on alumina, tin and zinc were carried out in exactly the same manner as outlined with similar experiments with acid green. The results of the work are given in Table VIII.

TABLE VIII

Azo-geranine—Alumina

Run	Dye solution Am't Dye	Am't Water	Orig. Conc.	Equil. Conc.	Adsorption
1	1 cc	59 cc	0.002 g	0.0003 g	0.0017 g
2	5	55	0.010	0.001987	0.008013
3	15	45	0.030	0.0075	0.0225
4	25	35	0.050	0.0132	0.0368
5	50	10	0.100	0.0426	0.0574
6	60	0	0.120	0.0609	0.0591

Azo-geranine—Tin mordant

7	1 cc	59 cc	0.002 g	0.000835 g	0.001165 g
8	5	55	0.010	0.00366	0.00634
9	15	45	0.030	0.0109	0.0191
10	25	35	0.050	0.0208	0.0292
11	50	10	0.100	0.0595	0.0405
12	60	0	0.120	0.0773	0.0427

Azo-geranine—Zinc mordant

13	1 cc	59 cc	0.002 g	0.00139 g	0.00061 g
14	5	55	0.010	0.0038	0.0062
15	15	45	0.030	0.0134	0.0166
16	25	35	0.050	0.0260	0.0240
17	50	10	0.100	0.0685	0.0315
18	60	0	0.120	0.0867	0.0333

Curves (Fig.4) were plotted and the maximum adsorption on the curve for zinc is represented by the line C, for tin by line D and for alumina by E. The adsorption values for the lakes as originally prepared fall on the 0.0120 g line (line B) of the curves.

The chemical potential may be expressed graphically for the dye on zinc as AB/AC; for tin as AB/AD and for alumina as AB/AE.

Evaluating these expressions we have:

Chemical potential for dye on Zn = AB/AC = 120/340 = .353
,, ,, ,, ,, ,, Sn = AB/AD = 120/430 = .279
,, ,, ,, ,, ,, Al = AB/AE = 120/610 = .197

Therefore, from the study of the chemical potential, the azo-geranine on zinc should fade faster than on tin, which in turn should fade faster than on alumina, because the chemical potential of the dye on the mordants is in that order.

Preparation of Alkali Blue Lakes.

(a) *Aluminum Lake*—This has been shown before.

(b) *Chromium, Tin, Zinc and Copper Lakes*—These were all prepared by adding 40 cc of the alkali blue solution, which was heated for fifteen minutes,

to the mordant and precipitating with 0.08 g of aluminum sulphate (iron free) dissolved in 5 cc of water. The amounts of the mordants used were—10 cc of chromium, 25 cc of tin, 13 cc of zinc and 5 cc of copper—all equivalent as the anhydrous oxides to the weight of 25 cc of alumina, calculated as Al_2O_3.

The iron lake was not comparable in shade to the other lakes, hard to grind and unsatisfactory for printing.
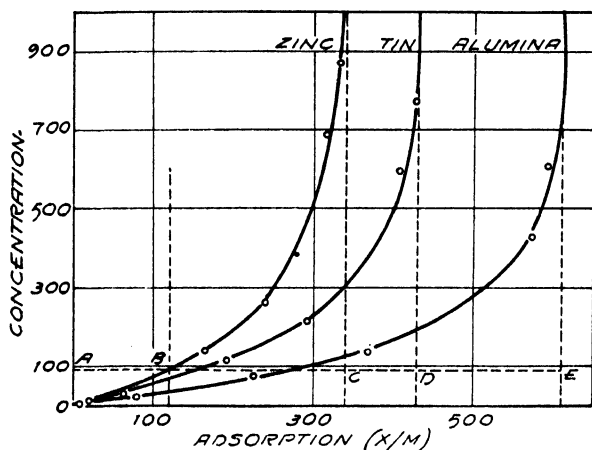
FIG. 4
Azo-Geranine Adsorption Curves

Results of Fading on the Alkali Blue Lakes.

TABLE IX

1. The aluminum lake fades completely in 35 hours.
2. The tin lake fades completely in 24 hours.
3. The zinc lake fades completely in 24 hours.
4. The chromium lake fades completely in 42 hours.
5. The copper lake changes color but does not fade completely in 43 hours.
6. The iron lake was not printed.

The alkali blue lakes of alumina, tin and zinc fade in less time than the chromium and copper lakes which shows that the lakes on colored mordants are less sensitive to light than those on the colorless mordants.

The greater resistance to light for the colored mordant lakes of alkali blue is similar to the acid green work. An alumina print behind the red glass will fade in approximately the same time as behind the colorless glass, while one behind the blue glass will resist the bleaching action of light for a much longer time. The blue glass acts like the colored mordants and cuts off the most effective rays, while the red glass transmits them.

The alkali blue fading results show that the zinc and tin lakes bleach in approximately the same time, and the alumina lake is faster to the action of light. If we again apply the chemical potential to explain these results, adsorption experiments for the dye on the three mordants must be run.

Adsorption Experiments for Alkali Blue.

Adsorption curves were prepared for alkali blue on alumina, tin and zinc, using the same method as described for the adsorption experiments of acid green. The results are given in Table X.

TABLE X

Alkali blue—Alumina mordant

| | Dye solution | | | | |
Run	Am't Dye	Am't Water	Orig. Conc.	Equil. Conc.	Adsorption
1	1 cc	59 cc	0.002 g	0 g	0.002 g
2	5	55	0.010	0	0.010
3	15	45	0.030	0.000697	0.029303
4	25	35	0.050	0.0075	0.0425
5	50	10	0.100	0.0418	0.0582
6	60	0	0.120	0.0595	0.0605

Alkali blue—Tin mordant

7	1 cc	59 cc	0.002 g	0.000736 g	0.001264 g
8	5	55	0.010	0.000923	0.009077
9	15	45	0.030	0.0119	0.0181
10	25	35	0.050	0.0260	0.0240
11	50	10	0.100	0.0548	0.0452
12	60	0	0.120	0.0706	0.0494

Alkali blue—Zinc mordant

13	1 cc	59 cc	0.002 g	0 g	0.002 g
14	5	55	0.010	0	0.010
15	15	45	0.030	0.00967	0.02033
16	25	35	0.050	0.0204	0.0296
17	50	10	0.100	0.0508	0.0492
18	60	0	0.120	0.0668	0.0532

Curves (Fig. 5) were plotted, and the maximum adsorption on the curve for tin is represented by the line C; the zinc maximum adsorption is approximately at the same point; and for alumina is represented by D.

The chemical potential may be expressed graphically for Sn as AB/AC; for Zn as AB/AC and for alumina as AB/AD. Evaluating these ratios we have for the various chemical potentials:—

$$Sn = AB/AC = 320/525 = .61$$
$$Zn = AB/AC = 320/525 = .61$$
$$Al = AB/AD = 320/630 = .508$$

Therefore, the expressions for the chemical potential of the dye on the three mordants show that the zinc and tin lakes should fade in about the same time, with which the experimental facts are in agreement, and the alumina lake should be less sensitive to light than either the tin or zinc lakes, which was the case.
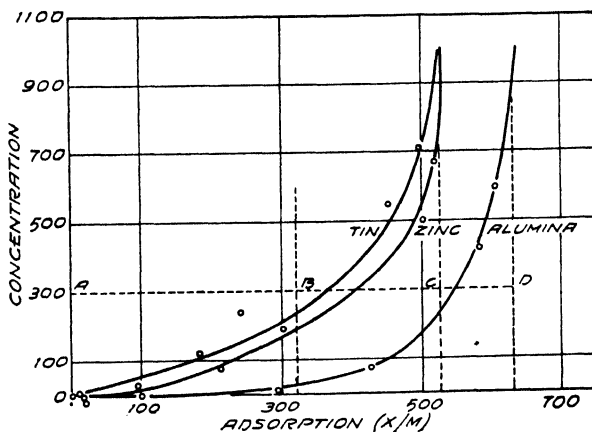
FIG. 5
Alkali Blue Adsorption Curves

Summary

The work on acid green, azo-geranine and alkali blue lakes has brought out the fact that dyes adsorbed on the mordants of iron, chromium and copper lakes are less sensitive to fading than on alumina, zinc and tin mordants. This is primarily true because the colored mordants act as screens preventing some of the damaging rays from acting on the dye.

With the colorless mordants, the chemical potential of the dye on the mordant governs the rate at which the lake will fade. With the three mordants used—alumina, tin and zinc, and the three acid dyes the order of fading is not always the same.

"The adsorption[1] of dyes by hydrous alumina, stannic oxide, and other mordants, as they are called, is of great importance in dyeing. Here as in all other cases the adsorption is selective."

Therefore we can not predict how fast a lake will be unless we know the mordant which is to adsorb the dye, and the chemical potential of the dye when adsorbed. However, this need not trouble the lake maker, for the two chief mordants of the basic class are alumina and chrome, and in general the alumina lakes will fade faster when exposed to the light. The dyer is more concerned with the problem, for his use of mordants is wider, and the solution for him is to determine the chemical potential of the dye on the fiber or mordant that he intends to use.

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[1] Bancroft: "Applied Colloid Chemistry," 108 (1926).

Alizarin Lakes

These lakes do not bring out the theory as well as the other experiments, for the alizarin is such a fast dye that the times of exposure to effect fading are so long that comparison is difficult. Also the dye does not give the same color with each mordant. However, from the results obtained we may draw a few conclusions which support the other work.

Preparation of Alizarin Lakes.

(a) *Aluminum Lake*—To 50 cc of the alumina were added 15 cc of a sodium alizarate solution, containing 2.88 gms per liter and 3 cc of a 0.01 N calcium acetate solution. The color of this lake was bright red.

(b) *Chromium Lake*—Prepared in the same manner but 20 cc of the chromium mordant, equivalent to the weight of 50 cc alumina weighed as Al_2O_3, were used as mordant. The color was purple.

(c) *Iron Lake*—Prepared in the same manner, but 25 cc of the hydrous iron oxide, equivalent to the weight of 50 cc of alumina, were used. The color of this lake was violet-black.

(d) *Tin Lake*—Prepared in the same manner, but 50 cc of the tin mordant, equivalent to 50 cc of the alumina were used. The color of the lake was orange.

(e) *Zinc Lake*—Prepared similar to the alumina lake, but 25 cc of the hydrous zinc oxide, equivalent to 50 cc of alumina, were used. The lake was lavender.

(f) *Copper Lake*—Prepared in the same manner, but 9 cc of copper mordant, equivalent to 50 cc of alumina, were used. The color of this lake was a dull violet.

The prints were prepared as shown with the lakes of acid green and were then exposed to the light of the Fade-ometer.

The Results of Fading on Alizarin Lakes.

TABLE XI

1. The aluminum lake fades completely in 73 hours.
2. The tin lake fades completely in 235 hours.
3. The zinc lake fades completely in 57 hours.
4. The chromium lake fades completely in 27 hours.
5. The copper lake fades nearly completely in 310 hours.
6. The iron lake was exposed for a total of 328 hours, but was not faded completely in this time.

The chromium and zinc fadings do not confirm the results of Stobbe,[1] who found that alizarin dyes fade more quickly on zinc mordant than on chrome mordant. Our results indicated that the reverse was true. To be absolutely sure of this, one would have to know the way his lakes were prepared, what the dye was, and the manner of forming the lake.

[1] Z. Elektrochemie, **14**, 480 (1908).

Our results do not seem to fall in line with the other experiments as far as the chrome lake is concerned, and also the differences in fading times are quite marked. The colors with alizarin and the various mordants are red with alumina, orange with tin, lavender with zinc, dull violet with copper, purple with chrome, and deep violet-black with iron. Hence they do not absorb the same rays and will not be affected in the same manner when exposed to the carbon arc light. This is similar to the idea of the colored mordants acting as screens. Also alizarin is so stable to light that it makes the results difficult to compare.

That the alumina lake in this case is more stable to light than the chromium and zinc lakes must mean that for the amount of dye used, the adsorption on the chromium and on the zinc are nearer the saturation values or maximum adsorptions than the alumina lake. The chemical potential for the dye on the chromium is greater than that for zinc, and the aluminum is the smallest.

The iron and copper lakes fade in about the same time and are much more stable than the lakes on the colorless mordants. This again proves that the lakes on colored mordants (chromium excepted in this case) are less sensitive to the action of light than the lakes prepared from the colorless mordants.

Conclusions

1. Methyl violet and methylene blue (basic dyes) fade in the absence of oxygen and air when exposed to the carbon arc light.

2. Acid green and alkali blue (acid dyes) fade in the absence of air or nitrogen.

3. It is possible, though not proved, that this bleaching is due to a rearrangement of the molecules in the dye. It may be a simultaneous oxidation and reduction.

4. Wool dyed with indigo is faster to the action of light than dyed cotton, because the chemical potential for the dye adsorbed on the wool is less than when it is adsorbed on cotton.

5. From baths of equal concentration the wool adsorbs more indigo than cotton per unit weight and will take longer to bleach.

6. The larger the amount of indigo adsorbed on cotton per unit area, the longer the time necessary in exposure to the Fade-ometer to effect fading.

7. Dyes are less stable to light than the corresponding lakes as shown by the experiments on alkali blue and azo-geranine (alumina lakes); magenta and methyl violet (tannic acid lakes).

8. Alkali blue and azo-geranine are not bleached by hydrogen peroxide as much as by the carbon arc light in the same period of time.

9. Hydrogen peroxide fades methyl violet and magenta, but the corresponding tannin lakes are only slightly affected.

10. Hydrogen peroxide fades magenta in less time than methyl violet, although the fading by the Fade-ometer light is the reverse.

11. Tannic acid darkens on exposure to the carbon arc light, which accounts for the lakes darkening instead of fading.

12. Lakes made from the colored mordants are more stable to light than those from the colorless mordants as shown by the experiments on acid green, azo-geranine, alkali blue and alizarin. This is because the colored mordants acting like color screens cut off some of the effective rays.

13. With the colorless hydrous oxides, the chemical potential of the dye adsorbed on the mordant governs the rate at which the lake will fade.

14. The ageing of a mordant will affect the adsorption, the chemical potential of the dye on the mordant, and consequently the time of exposure necessary to cause fading.

15. Acid green precipitated on alumina by barium chloride is more stable to light than the lake precipitated by means of lead acetate.

Acknowledgment

THE DISTRIBUTION RATIOS OF SOME FATTY ACIDS AND THEIR HALOGEN DERIVATIVES BETWEEN WATER AND OLIVE OIL[*]

BY MEYER BODANSKY AND ARCHIBALD V. MEIGS

The data presented in this paper were obtained in connection with a study of the hemolytic action of fatty acids and their halogen derivatives. Although the general problem of the penetration of these compounds through cell membranes has been the subject of several investigations and although attempts have been made to correlate the cellular permeability of these substances with their solubility in lipoids, extremely little information is actually available regarding their solubility in fats and fat-like substances.

Perhaps the most extensive analyses which have some bearing on the problem are those of Smith and White[**] who determined the distribution ratios of various organic acids, including certain fatty acids and their halogen derivatives, between water and the fat solvents, toluene, benzene and chloroform. Taylor[2] determined the distribution coefficients of several acids between water and olive oil, and in an earlier paper the present writer[3] presented similar data for the saturated fatty acids, from formic to pelargonic. In these determinations, however, the ratio of oil to water was 1:15.

In the analyses upon which the present data are based, equal volumes of oil (Squibb) and aqueous solutions of the fatty acids were used and the work extended to include several halogen derivatives which were of particular interest from the standpoint of our studies on hemolysis.

In determining the distribution of an acid between two solvents in one of which it dissociates, it is obviously necessary to take into account the dissociation of single molecules into ions in that layer, the true partition coefficient (in our case) being the ratio of the concentration of the undissociated acid in the aqueous layer to the concentration of the acid in the olive oil. Representing the true partition coefficient by P, it is determined from the formula:

$$P = \frac{C_o n^2 - C_o' N^2}{(n - N)nN}$$

C_o is the millimolecular concentration of the fatty acid in the oil layer and C_o' the lowest millimolecular concentration (in the same layer) that is not an aberrant value.[1]

[**] Owing to technical limitations a high degree of accuracy in the titrations cannot be expected in very low concentrations. Accordingly, as described by Smith and White, aberrant values are eliminated by plotting the experimentally determined values of C_o/N^2 and $1/N$. Those values of C_o/N^2 are disregarded which are not consonant with the majority and a value of C_o/N^2 chosen to serve as a basic term of the series from which to calculate the successive values of P.

$N = C_w(1-\alpha)$, where C_w is the millimolecular concentration in the aqueous layer and $(1-\alpha)$ is calculated from Ostwald's dilution law. (For this purpose the dissociation constants used were those given by Scudder[4] and in the International Critical Tables, Vol. VI).

Also, $n = C_w'(1-\alpha')$, where C_w' is the lowest non-aberrant value of C_w in the series and α' the lowest value of α in the series. The steps in the determination of the value of P for one of the compounds, namely, valeric acid, are outlined in Table I.

TABLE I

The Partition Coefficient of Valeric Acid between Water and Olive Oil at 25°C

Approximate normality	C_t	C_w	C_o	K 10^{-5}	V	$KV =$ $\alpha^2/1-\alpha$ 10^{-4}	α	$1-\alpha$	$N =$ $C_w(1-\alpha)$ -3	N^2 -4
0.1	96.0	26.0	70.0	1.56	38.5	6.0	0.024	0.976	25.6	6.55
0.05	48.7	13.7	35.0		73.0	11.4	0.033	0.967	13.25	1.75
0.02	19.8	5.8	14.0		172.0	26.9	0.051	0.949	5.5	0.303
0.01	9.6	2.6	7.0		385.0	60.2	0.075	0.925	2.40	0.0575
0.005	4.8	1.3	3.5		770.0	120	0.100	0.900	1.17	0.0137

Approximate normality	$1/N$	C_o/N^2	$-(n-N)$ -3	nN -6	$(n-N)Nn$ -7	$C_2'N^2$ -7	C_on^2 -7	$-(C_on^2-C_o'N^2)$ -7	P
0.1	39	106.8	24.43	30.0	7.32	22.9	0.96	21.94	2.995
0.05	75.5	200.0	12.08	15.5	1.875	6.1	0.48	5.62	3.00
0.02	182	463.0	4.33	6.44	0.279	1.06	0.19	0.87	3.12
0.01	417	1217.0	1.23	2.81	0.0345	0.201	0.96	0.105	3.04
0.005	855	2555.0	—	—	—	—	—	—	—

Values of P have not been computed for all compounds. In several instances there were not available in the literature dissociation constants upon which to base the calculation. In other cases the series of concentrations was limited to the range used in the studies of hemolysis, and particularly with several of the halogen derivatives it was necessary to exclude most of the data for low concentrations, owing to a shifting end-point in the titration with alkali. Direct determination of the halogen content in these cases was attempted, but the results were not entirely satisfactory.

In Tables I and II, C_t is the total initial concentration of the fatty acid in the aqueous layer, in millimols per liter; K is the dissociation constant, and $V = 1/C_w$ (i.e., the volume of water in liters containing 1 mol of the fatty acid). The significance of the terms C_o, C_w, N, and n has already been stated.

TABLE II

	C_t	C_w	C_o	C_w/C_o	C_o/C_w	P
Acetic acid	206.4	197.0	9.4	20.9	0.0477	
25°C.	101.0	96.0	5.0	·19.2	0.0525	
$K = 1.813 \times 10^{-5}$	50.4	49.2	1.2	41.0	0.0244	
	10.3	10.2	0.1	102.0	0.0083	
37.5°C.	202.6	193.0	9.6	20.1	0.0497	
	101.6	96.2	5.4	17.8	0.0561	
	50.4	49.2	1.2	41.0	0.0244	
	10.3	10.2	0.1	102.0	0.0083	
Chloracetic acid	203.0	185.0	18.0	10.27	0.0973	0.0758
25°C.	101.8	92.8	9.0	10.31	0.0970	0.0817
$K = 1.52 \times 10^{-3}$	9.8	9.2	0.6	15.30	0.0652	
37.5°C.	98.5	89.5	9.0	9.95	0.1005	
	48.5	45.5	3.0	15.15	0.0645	
	18.5	17.5	1.0	17.50	0.0572	
	9.7	9.2	0.5	18.40	0.0543	
Bromacetic acid	199.0	169.0	30.0	5.63	0.178	
25°C.	99.2	87.8	11.4	7.70	0.130	
$K = 1.35 \times 10^{-3}$	200.0	178.0	22.0	8.10	0.1235	
37.5°C.	99.8	93.8	6.0	15.60	0.0640	
Iodoacetic acid	99.5	74.5	25.0	2.98	0.336	
37.5°C.	49.5	35.5	14.0	2.54	0.394	
$K = 7.1 \times 10^{-4}$	19.5	14.5	5.0	2.90	0.345	
at 25°C.						
Dichloracetic acid	103.8	82.2	21.6	3.80	0.262	
25°C.	51.0	44.0	7.0	6.30	0.159	
$K = 5.7 \times 10^{-2}$						
37.5°C.	93.5	75.5	18.0	4.19	0.239	
	46.5	39.5	7.0	5.64	0.177	
Trichloracetic acid	99.8	82.0	17.0	4.60	0.217	(at 25°C.)
	101.6	79.2	22.4	3.53	0.283	(at 37°C.)
Propionic acid	254.0	218.0	36.0	6.25	0.165	0.162
25°C.	202.0	173.0	29.0	5.97	0.1675	0.163
$K = 1.32 \times 10^{-5}$	101.4	87.0	14.4	6.04	0.1655	0.169
	50.2	43.0	7.2	5.96	0.1674	0.157
	20.4	17.6	2.8	6.28	0.1590	
37.5°C.	252.0	209.0	43.0	5.19	0.206	0.2485
	199.6	168.0	31.6	5.32	0.188	0.2690
	101.5	83.0	18.5	4.49	0.223	0.2620
	50.2	40.6	9.6	4.23	0.237	

TABLE II (Continued)

	C_t	C_w	C_o	C_w/C_o	C_o/C_w	P
β–Chloropropionic	192.0	149.0	43.0	3.47	0.289	0.333
acid, 25°C.	95.6	74.0	21.6	3.43	0.292	0.296
$K = 8.4 \times 10^{-5}$	17.2	14.0	3.2	4.56	0.229	
37.5°C.	191.0	153.0	38.0	4.03	0.248	
	95.0	74.4	20.6	3.61	0.277	
	18.64	15.5	3.14	4.94	0.203	
α–Bromopropionic	192.0	125.0	67.0	1.87	0.536	0.660
acid, 25°C.	101.4	65.0	36.4	1.785	0.560	0.656
$K = 1.06 \times 10^{-3}$	47.8	31.0	16.8	1.845	0.542	0.654
37.5°C.	201.0	136.0	65.0	2.09	0.478	
	101.0	69.0	32.0	2.155	0.464	
β–Bromopropionic	206.0	140.0	66.0	2.12	0.472	0.457
acid, 25°C.	102.0	69.4	32.6	2.13	0.470	0.458
$K = 9.5 \times 10^{-5}$	50.8	33.8	17.0	1.99	0.502	
Butyric acid	202.0	120.0	82.0	1.46	0.684	0.594
25°C.	101.0	61.0	40.0	1.52	0.656	0.596
$K = 1.5 \times 10^{-5}$	48.8	30.8	18.0	1.71	0.584	0.620
	19.8	12.5	7.3	1.71	0.584	
37.5°C.	201.0	119.0	82.0	1.45	0.689	0.650
	100.0	60.0	40.0	1.50	0.667	0.654
	49.6	30.6	19.0	1.61	0.622	0.672
	20.6	12.6	8.0	1.58	0.634	
Isobutyric acid	203.0	118.0	85.0	1.39	0.719	0.737
25°C.	102.0	62.0	40.0	1.55	0.645	0.750
$K = 1.55 \times 10^{-5}$	49.4	31.0	18.4	1.68	0.594	
37.5°C.	204.0	118.0	86.0	1.38	0.727	0.808
	102.0	61.0	41.0	1.49	0.672	0.920 (?)
	50.0	30.0	20.0	1.50	0.667	0.834
α–Bromobutyric	213.0	88.0	125.0	0.704	1.42	1.37
acid 25°C.	104.6	45.6	59.0	6.77	1.29	1.39
$K = 1.03 \times 10^{-3}$						
Valeric acid	96.0	26.0	70.0	0.372	2.70	3.00
25°C.	48.7	13.7	35.0	0.392	2.56	3.00
$K = 1.56 \times 10^{-5}$	19.8	5.8	14.0	0.415	2.41	3.12
	9.6	2.6	7.0	0.371	2.69	3.04

<div align="center">TABLE II (Continued)</div>

	C_t	C_w	C_o	C_w/C_o	C_o/C_w	P
37°C.	97.4	26.0	71.4	0.365	2.74	3.00
	48.5	13.5	35.0	0.385	2.60	3.00
	19.5	5.5	14.0	0.393	2.55	3.07
	9.6	2.6	7.0	0.371	2.70	3.04
	4.8	1.3	3.5	0.371	2.70	
Isovaleric acid	100.8	32.0	68.8	0.465	2.15	1.80
25°C.	48.7	16.7	32.0	0.522	1.92	2.04
$K = 1.68 \times 10^{-5}$	19.2	7.0	12.2	0.574	1.74	1.86
37.5°C.	100.6	31.8	68.8	0.463	2.16	1.79
	49.0	32.0	17.0	0.532	1.88	1.805
	19.3	7.1	12.2	0.582	1.72	1.87
	9.5	3.5	6.0	0.583	1.92	
α–Bromovaleric	106.0	20.0	86.0	0.233	4.30	
acid 25°C.	52.3	10.3	42.0	0.245	4.08	
	21.8	4.8	17.0	0.283	3.58	
37.5°C.	104.0	19.0	85.0	0.223	4.49	
	52.2	10.2	42.0	0.243	4.12	
	21.5	4.5	17.0	0.265	3.77	
α–Bromoisovaleric	106.2	22.2	84.0	0.265	3.78	
acid, 25°C.	53.0	13.0	40.0	0.325	3.08	
	19.3	5.3	14.0	0.379	2.64	
	9.2	3.2	6.0	0.532	1.87	
37.5°C.	105.2	22.2	83.0	0.268	3.74	
	49.0	12.0	39.0	0.308	3.25	
	20.3	6.3	14.0	0.45	2.22	
Caproic acid	49.6	5.6	44.0	0.127	7.88	
25°C.	19.4	2.4	17.0	0.141	7.10	
$K = 1.46 \ 10^{-5}$	9.4	1.2	8.2	0.146	6.85	
37.5°C.	50.6	6.6	44.0	0.165	6.03	
	19.7	2.7	17.0	0.159	6.29	
	9.5	1.3	8.2	0.159	6.29	

References

[1] H. W. Smith, and T. A. White: The distribution ratios of some organic acids between water and organic liquids, J. Phys. Chem., **33**, 1953 (1929).

[2] N. W. Taylor: The nature of the nerve receptor for the acid taste as indicated by the absorption of organic acids by fats and proteins, Protoplasma, **10**, 98 (1930).

[3] M. Bodansky: Lipoid solubility, permeability and hemolytic action of the saturated fatty acids, J. Biol. Chem., **79**, 241 (1929).

[4] "The Electrical Conductivity and Ionization Constants of Organic Compounds" (1914).

SOLUTION AND DE-SOLUTION OF CELLULOSE ESTERS BY HOMOLOGOUS SERIES OF CARBON COMPOUNDS*

BY S. E. SHEPPARD AND S. S. SWEET

The solubility of cellulose esters in organic solvents, simple and mixed, has been the subject of numerous investigations, both practical and theoretical. Quantitative treatment of the subject, according to phase rule principles, is impeded by a number of factors, mostly those inherently characterizing so-called "high molecular" substances. Thus, the question as to whether the "solutions" are molecular or micellar is still a vexed one,[1] although it may be said that the evidence that many of the typical "high molecular" bodies form true molecular solutions at sufficient dilution is increasing. In any case, the existence of limited solubilities, corresponding to the saturated equilibrium systems of small molecular weight bodies, can only be predicated with great reserve and is not readily demonstrated, although a good case is made out for it by Mardles.[2] The solubility phenomena for the cellulose esters are compli-cated, among others, by the following important factors:

(a)   Nature of ester radicle: putting the nitrates in one division, we have a homologous series of compounds (normally) in the cellulose esters of the aliphatic acids. The marked change in general solubility phenomena as we pass:

Cellulose formate→acetate→laurate→stearate has been frequently noted, there being a roughly progressive tendency to solution in liquids of lesser polarity.[3] The marked influence which the polar hydroxyl group has upon the solubility is shown in the properties of the cellulose esters of hydroxy organic acids, prepared by C. Staud, et. al.,[4] and which show solubility in water. This is probably related to the water solubility shown by certain cellulose ethers (lower than the triether) and is perhaps dependent upon the formation of oxonium hydrates.[5]

(b)   Confining attention, however, to cellulose esters of a single acid, solubility conditions again vary markedly but fairly regularly with the degree of esterification. The most typical substances here are the tri-esters; the great changes with degree of esterification are illustrated in the following comparative solubility ranges for *cellulose acetates* of *different acetyl content* in binary solvent mixtures of normal alcohols with ethylene dichloride. (Figs. 1 and 2). Diagrams for chloroform-alcohols, tetrachlorethane-alcohols are very similar. In each case we note that the solubility range *diminishes* with increas-ing molecular weight of the alcohol, and that as the tri-ester is approached, solubility is less in the more polar mixture. (Cellulose triacetate is soluble in tetrachlorethane, and chloroform but insoluble in ethylene dichloride).

FIG. I
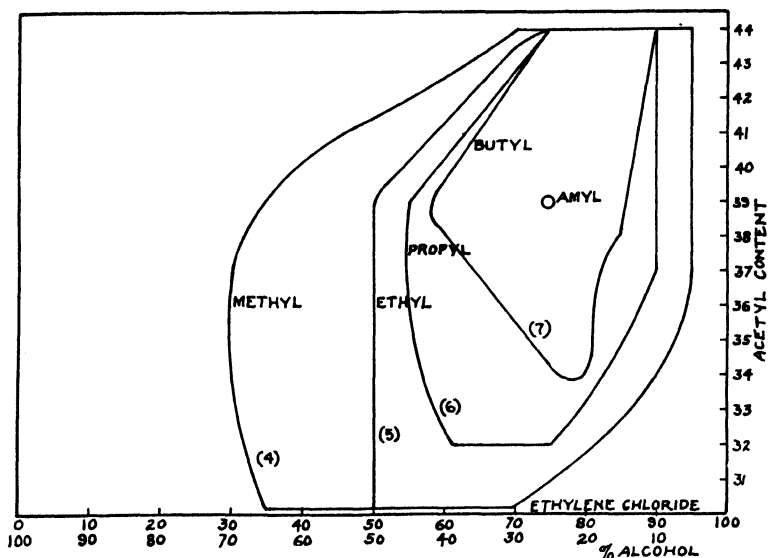
(c)   A single-valued ester, of definite acyl composition, is not, however, a unique compound, but usually a mixture of portions of differing molecular weights, and corresponding physical properties.   This has been shown for cellulose nitrate[6] and cellulose acetate.[7]   McNally and Godbout, in our laboratory, found that "the fractions of cellulose acetate which precipitate first from an acetone-water mixture are more insoluble in solvents in general than are those which precipitate later."   It is possible that this increase in the
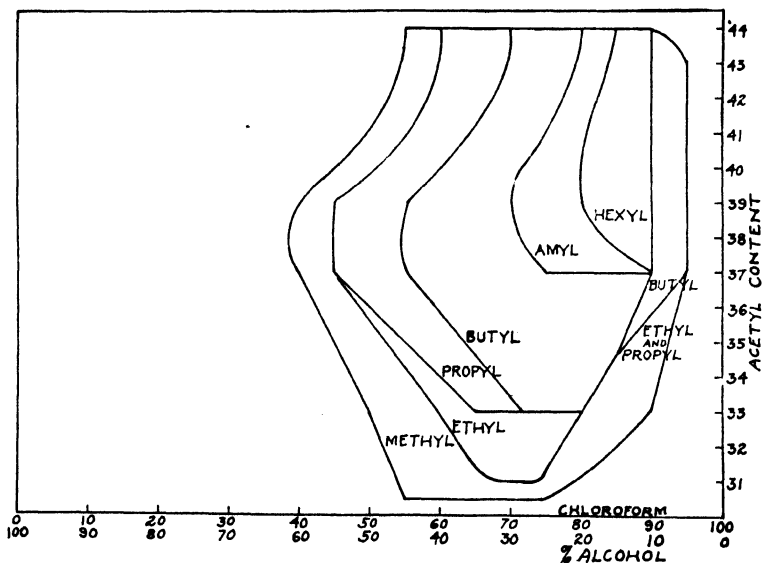
FIG. 2

general solubility range with diminished molecular weight is dependent upon the greater influence of unsaturated end-groups as the length of the primary valence chain is diminished.[8] For evidence that the fractions of a cellulose acetate, of constant acetyl content, represent different molecular weights, reference may be made to recent papers by H. Staudinger.[9] These conditions show first, with what reserve we must receive statements on the solubilities of cellulose esters, and second, point to the conditions to be secured for more definitive data. Most of the data on solubilities of cellulose esters are for polydisperse (*i.e.* polyhomologous) mixtures, of which generally not even the average state of aggregation, or molecular weight is specified. The fact that the general range of solubility increases with degradation, or molecular weight lowering, shows that comparison of solubilities of *different* cellulose esters, *e.g.*, of different aliphatic acids, should be made for materials of:

 (a)   equivalent degree of esterification (acyl content),
 (b)   identical average degree of degradation (molecular weight),
 (c)   equal homogeneity, *i.e.*, narrow range of fractionation.

We wish that we could say that the data to be presented in this paper fulfilled these conditions, but must be content to suggest the better path. The method of ascertaining the factors under (b) and (c) is from study of the viscosity: concentration curves for concentrations which give purely viscous flow uncomplicated by plasticity.[10]

Relative Solubility Indications

If we cannot, as yet, specify solubility in terms of molar concentration in equilibrium with a solid phase, and *independent* of the amount of the *solid phase*[11] at a given temperature, what are we to take as a solubility index?

The chief contribution to this has been made by E. W. J. Mardles[12] from whose work largely the use of the so-called "dilution ratio" has been derived. The method, at constant temperature as given by Mardles, consists in adding a non-solvent (diluent, precipitant) from a burette, to about 5 cc. of a solution (of specific concentration of cellulose ester in a definite solvent, *e.g.*, 5 per cent). There is observed the amount required to produce initial turbidity. After each addition the mixture is shaken some minutes, until a drop or two produces just perceptible permanent turbidity—in some cases opalescence.

Mardles defines the solvent power number as "the volume of the liquid (diluent) in cubic centimeters required to begin precipitation from 1 cc. of a 5 per cent solution." From this the dilution ratio (from cellulose nitrate) has been derived[13] as

$$\frac{V_d}{V_n} = D.R.$$

Where V_d = added volume of diluent

V_n = initial volume of solvent.

and specific conditions instituted, *e.g.*, for nitrocellulose lacquer control, two grams "half-second" cellulose nitrate dissolved in 20 cc. of solvent. The volume of diluent at 20°C., divided by the volume of the solvent, represents the *dilution ratio*.[14]

Since the system is neither one of constant total molar concentration (of cellulose ester) on volume normal basis nor on weight normal basis, it might be regarded as of only approximately practical utility to measure dilution ratios, and not leading to wider scientific values. Mardles has shown, however, that it is adapted to exhibiting a variety of characteristic solvent power differences between different types of organic solvents in relation to a given cellulose ester.

The following data are given in illustration of this, and particularly in following up the observation of Mardles.[15] "It is invariably the rule [for cellulose nitrate] that there is a rapid decrease in solvent power with ascent in any homologous series." "Similarly, it has been shown that with rise in any homologous series, the relative volume required to begin precipitation of the cellulose ester from solution decreases rapidly."

Our procedure, in the orienting experiments described, consisted in determining the volume, in cubic centimeters of diluent or precipitant, required for turbidity when added to 10 cc. of 5 per cent cellulose acetate (acetyl 40.2 per cent) dissolved in pure acetone. Instead of taking or plotting the solvent power or dilution ratio, we found it more convenient to express results in terms of its reciprocal, which we termed the *precipitating power* of the diluent. On plotting this against *molecular weight*, or number of carbon atoms, for homologous series, curves were obtained giving good approach to straight lines as the molecular weight increased beyond a certain value. The relation of these curves seemed adapted to more ready graphic comparison of the solvent and displacing properties of organic liquids for cellulose acetate of the composition, *etc.*, used.

Data for a series of compounds are illustrated in Figs. 3 and 4.

These cover:

Normal aliphatic hydrocarbons (paraffins)
C_nH_{2n+2} from C_5 to C_{10}

Normal aliphatic alcohols
C_nH_{2n+1} OH from C_1 to C_{16}

Normal fatty acids
C_nH_{2n+1} COOH from C_1 to C_{17}

Normal alkyl chlorides
C_nH_{2n+1} Cl from C_2 to C_5

Ethyl esters of fatty acids
C_nH_{2n+1} COOC$_2$H$_5$ from C_1 to C_{17}

Normal alkyl esters of acetic acid
CH_3 . COO . C_2H_{2n+1} from C_1 to C_{16}

Normal aliphatic aldehydes
C_2H_{2n+1} . CHO from C_1 to C_7

For these materials, the graphs indicate approach to a linear relation of the *precipitating power* to molecular weight,

$$P = a + b.M.$$

where a and b are constants, and M = molecular weight.
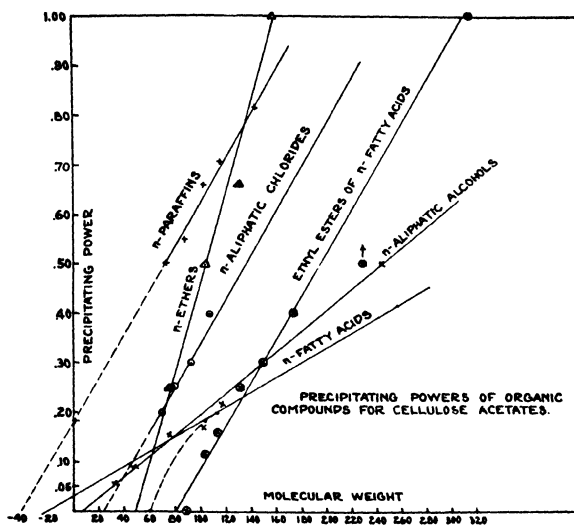
FIG. 3

The theoretical intercept a is a large negative quantity for the normal hydrocarbons (paraffins) and a small negative quantity for the normal fatty acids. If the linear relation held perfectly, this intercept represents the value of the molecular weight at which this type of compound commences to have solvent properties in conjunction with acetone. In most cases, however, the earlier members of a series diverge from the linear relation, and show solvent
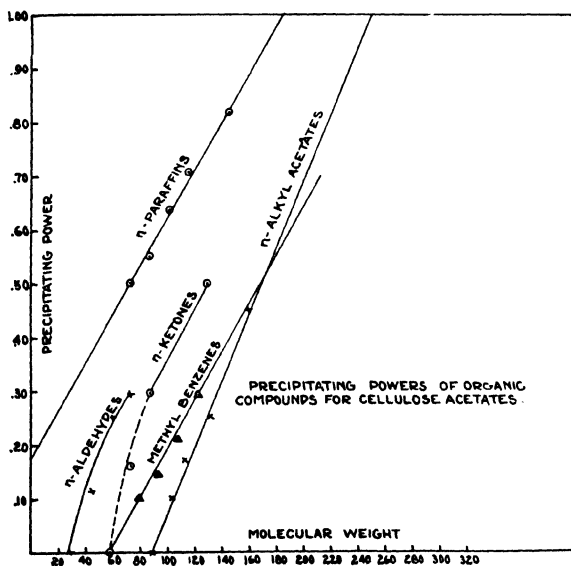
FIG. 4

properties at higher molecular weights than the theoretical intercept. In some cases the rule holds even to the first member (*e.g.*, ethyl esters).

The following intercepts and slope-constants were obtained:

TABLE I

Substance	Formula	a	$\Delta P/CH_2$ b
Paraffins	C_nH_{2n+2}	-40	1.842
n-alkyl chlorides	C_nH_{2n+1} Cl	$+24$	1.814
Ethyl esters of fatty acids	C_nH_{2n+1} COO Et	$+80$	1.770
n-alkyl acetates	CH_3 COO . C_nH_{2n+1}	$+86$	2.475
n-fatty acids	C_n . H_{2n+1} COOH	-20	0.582
n-alcohols	C_nH_{2n+1} OH	$+6$	0.582
n-(sym) ethers	$(C_nH_{2n+1})_2$ O	$+50$	3.732
	½ value	$+25$	2×1.86

The values of the slopes b correspond as $\Delta P/CH_2$ to the effect per CH_2 of chain lengthening to increase the precipitating, or inversely in diminishing, solvent power.   In the alkyl chlorides, ethyl esters, and ethyl ethers, this differs little from the value for paraffins.   In the alkyl acetates b is greater, but in the fatty acids and in alcohols, much lower.   This suggests an effect of the strongly polar OH and COOH groups.   The difference in slope for the n-alkyl acetates from the ethyl alkyl esters is rather peculiar, considering the similarity of the configurations

$$
\begin{array}{ccc}
& CH_3 & & R \\
& \diagup & & \diagup \\
C = O & \text{and} & C = O \\
& \diagdown & & \diagdown \\
& OR & & OCH_3
\end{array}
$$
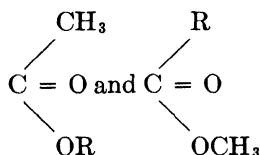
where $R = C_nH_{2n+1}$.

The values of b (or $\Delta P / [CH_2]$) for n-ketones and aldehydes, so far as the data permitted, also indicated close approach to the value for the paraffins, *etc.* Both the theoretical intercepts, and the actual values of M.W. for $P = 0$ show slightly greater solvent power for ketones than for aldehydes.

Further data on esters of homologous series of fatty acid esters are shown in Fig. 5, both on the molecular weight basis, and referred to number of C atoms of normal chains.   The constants from the graphs give:

TABLE II

Series	a	$b = \Delta P/\Delta CH_2$
Acetates	$+82$	1.036
Propionates	70	0.885
Butyrates	76	.852
Valerates	76	.824
Caproates	60	.754

The graphs are on a different scale from that of the other figures but indicate that the slope b. i. e., the effect of increasing M.W. by CH_2, diminishes steadily from the acetates to the caproates. It appears that the slope for the caproates is approaching that for the n. paraffins, so that the progression seems of regular character. Both the theoretical and actual intercepts
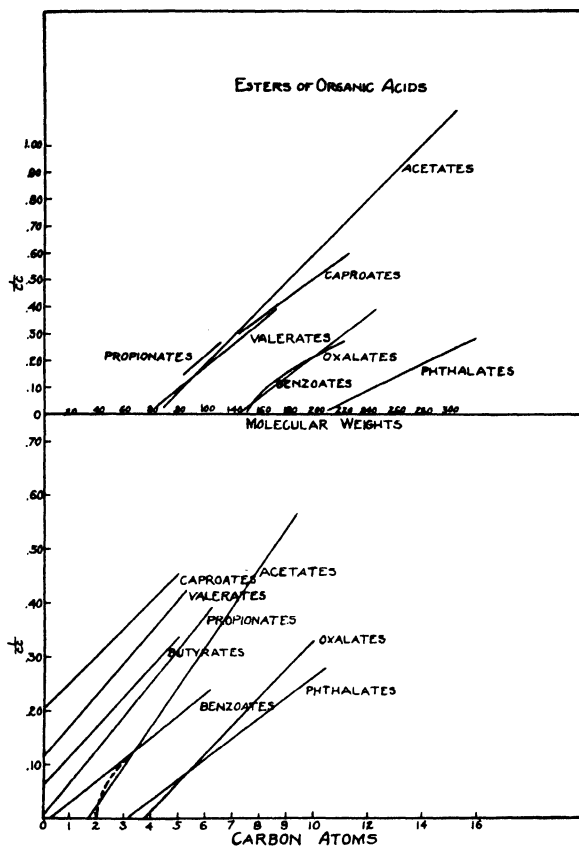
FIG. 5

(a-values) indicate little difference, on a molecular weight basis, in actual solvent powers, of the different series, but the b-values, and the plot in terms of number of C-atoms indicate that the compensation in the formula

$$R_2 - \overset{\overset{\displaystyle O}{\displaystyle \|}}{C} - O - R_1$$
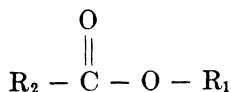
(where R_2, R_1 = alkyls) of R_2 and R_1 is not absolute, but that the alkyl united to the oxygen (R_1) has the greater moment or weight. Insufficient data were obtained on the formates, since all these below *amyl* formate were solvents, and members above were not available.

Data were also obtained for esters of dibasic acids. It is possibly not strictly permissible to compare dibasic acid esters with monobasic on a *molecular* weight basis, but effectively, whether equivalently or molecularly, the solvent power increases for the dibasic esters, as would be expected from the higher ratio of polar : non-polar grouping.

Aryl Compounds

In the methylated benzenes (Fig. 6) the advance was not in the side chain, but in the nucleus, the series being:

Substance	Formula	Vol.	P = 1/V
Benzene	$C_6 H_6$	10	0.10
Toluene	$C_6 H_5 . CH_3$	7	0.14
o.Xylene	$C_6 H_4 . (CH_3)_2$	4.5	0.22
Mesitylene	$C_6 H_3 . (CH_3)_3$	3.5	0.29

It is interesting that these also gave a linear relation of P to molecular weight. In the alkyl *benzoates*, the pro-solvent effect of the relatively unsaturated benzene ring is definitely shown, while the phthalates show a relation to the *benzoates* similar to that of oxalates, succinates, *etc.*, to monobasic esters. So far as a cellulose acetate still containing $-OH$ groups is concerned, increased relative solvent power is shown by the alkyl lactates and tartrates, compared with monobasic esters. The lactates up to butyl lactates were actual solvents. Hence, comparing

$$
\begin{array}{ccc}
H & & O \\
| & & \| \\
Me = CH & - & C - R \quad \text{Acetates}
\end{array}
$$

$$
\begin{array}{ccc}
OH & & O \\
| & & \| \\
Me - CH & & C - R \quad \text{Lactates}
\end{array}
$$
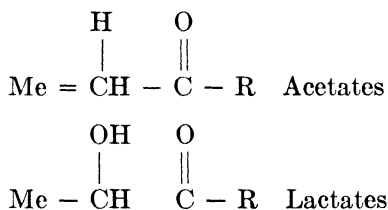
the solvent power is extended considerably by introduction of the polar $-OH$ group. Higher lactates were not available to test the difference term $\Delta P/[-CH_2]$ in this series. The alkyl tartrates, compared with oxalates, showed a similar displacement, but true comparison would be with *succinates,* of which insufficient data were available.

Oxalates
$$
\begin{array}{c}
O \\
\| \\
C - OR \\
| \\
C - OR \\
\| \\
O
\end{array}
$$

Succinates
$$
\begin{array}{cc}
H & O \\
| & \| \\
CH - & C - OR \\
| & \\
CH - & C - OR \\
| & \| \\
H & O
\end{array}
$$

Tartrates
$$
\begin{array}{cc}
OH & O \\
| & \| \\
CH - & C - OR \\
| & \\
CH - & C - OR \\
| & \| \\
OH & O
\end{array}
$$
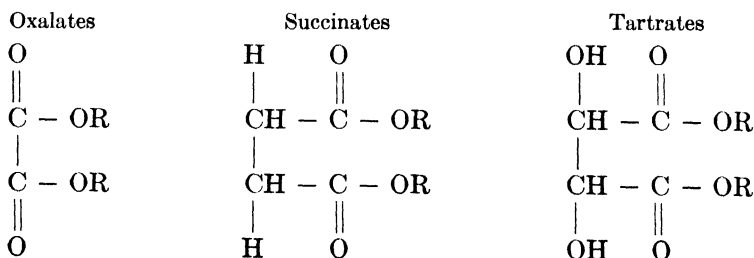
Isomerism and Branched Chains

With both alcohols and acetates it was observed that branching of the hydrocarbon chain reduced the precipitating power, *i.e.*, exalted the solvent power, *i.e.*, the solvent power order was:

$$\text{Tertiary} > \text{Secondary} > \text{Iso} > \text{Normal}$$

This is illustrated in the graph of Fig. 6.
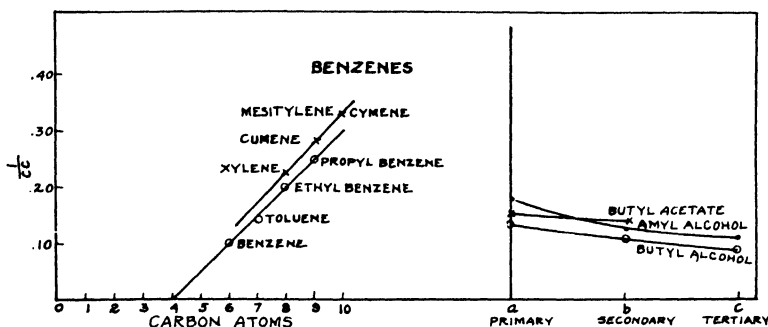
FIG. 6

Unsaturation

Not many experiments were carried out on this, but it appears that generally unsaturation increases relative solvent power for cellulose acetates (of acetone soluble type). This is shown on comparing benzene with hexahydrobenzene, and phenol with cyclohexanol.

TABLE III

Substance	Formula	Precipitating Power
Benzene	C_6H_6	0.10
Hexahydrobenzene	C_6H_{12}	0.33
Phenol	$C_6H_5.OH$	0.00 (Solvent)
Hexanol	$C_6H_{11}OH$	0.08

Solvent Mixtures and Cellulose Esters

The fact that certain pairs of organic liquids are much better solvents for various cellulose esters than either separately, and may indeed possess solvent properties when neither alone is a solvent, has been much discussed.[16] Without claiming that a completely adequate theory of cellulose ester solution is available, it appears that the polar:non-polar balance theory of Highfield[17] with certain modifications[18] is qualitatively satisfactory. The results presented here are in good accord therewith.

The general effect of water in changing the polarity balance of a solvent or solvent mixture, was discussed by Sheppard, Carver and Houck.[18] The effect of water on the solvent power of acetone plus diluent mixtures for acetone soluble cellulose acetate is illustrated in Fig. 7.
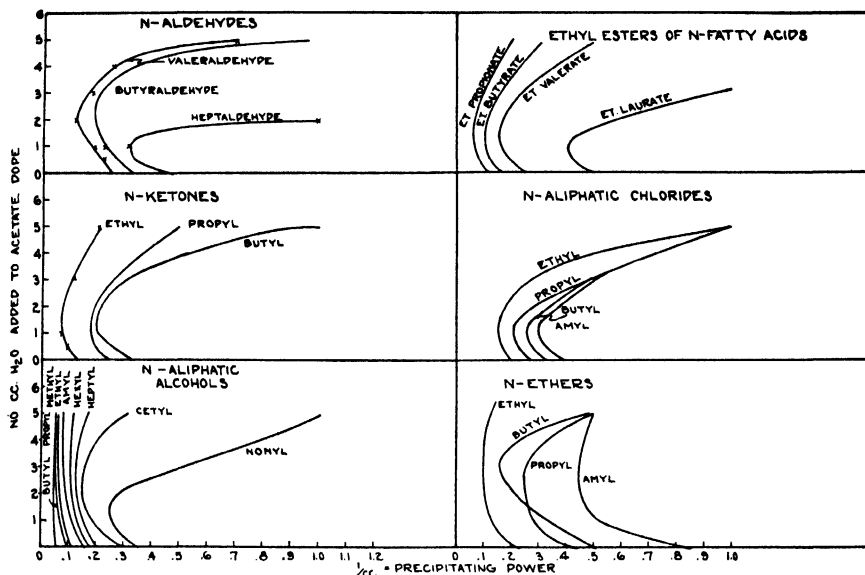
FIG. 7

The existence of a solvent power maximum for a specific concentration of water present is clearly brought out, thus confirming the results of viscosity and plasticity measurements.[10] More recently, valuable contributions to a more quantitative theory of swelling and solution of organic colloids have been made by Wo. Ostwald.[19] In particular, Sakurada[20] has discussed swelling data for cellulose acetate in relation to the polar moments of the liquids.

Ostwald's suggestion that the swelling power for rubber was given by the empirical rule

$$\varphi^{1/n} \epsilon = K \text{ (constant)}$$

where n lies between 2 and 3, and ϵ = dielectric constant, was found to have approximate validity only within the same homologous series. As now known, the dielectric constant *per se* is not a complete measure of molecular polarity. Sakurada found that swelling of an acetone soluble cellulose acetate increased with dipole moment.

The swelling power in a homologous series diminished with molecular weight, as found by Mardles for solvent power, and confirmed in the present report. Generally, and statistically, Sakurada found that nitrates for which μ/V (polar moment/molecular volume) was less than 10, were non-swelling agents, between 10 and 14 swelling but not solvent, and above 14 swelling and solvent agents. The alcohols (and water) fall out of line with this, but if the molecular volume is corrected for association, they return to the region of non-solvents. (The same appears to be true for the fatty acids. If we take the ratio of the slopes

$$b = \frac{\Delta P}{(-CH_2)}$$

for alcohols and fatty acids to paraffins, we have

$$\frac{1.84}{.84} = 2.2$$

for alcohols

$$\frac{1.84}{.58} = 3.2$$

for acids, which may indicate average association factors.)

The results presented here are to be regarded as orienting only. They indicate, however, that in the complex problem of the solubility of cellulose esters and the like, comparison of homologous series of compounds is likely to give more definite and intelligible information than comparison of individual compounds. "He who would sup with the devil needs a long spoon" and an increasing chain of $-CH_2$ groups provides a convenient handle to the actual spoon.

Summary

1. The factors involved in making definitive solubility measurements for cellulose esters are distinguished.

2. Quantitative comparisons of solvent and precipitating powers of homologous series of organic compounds with acetone soluble cellulose acetate disclose certain regularities. A linear relation to molecular weight is approached as molecular weight increases, and the comparison of the series behavior allows more general conclusions to be drawn as to effects of structure on solvent power.

Bibliography

[1] S. E. Sheppard: J. Rheology, 1, 471 (1930).
[2] E. W. J. Mardles: Kolloid-Z., 49, 4, 11 (1929).
[3] Cf. G. S. Whitby: Colloid Symposium Monograph, 4, 203 (1926).
[4] C. J. Staud and C. S. Webber: U. S. Patent No. 1, 785, 466.
[5] Cf. H. Staudinger et al.: Ber., 63, 2308 (1930).
[6] H. De Mosenthal: J. Soc. Chem. Ind., 30, 782 (1911).
[7] J. G. McNally and A. O. Godbout: J. Am. Chem. Soc., 51, 3095 (1929).
[8] Cf. H. Staudinger and I. Fritschi: Helv. Chim. Acta., 5, 785T (1922).
[9] Loc. cit., also, Ber., 63, 3132 (1930).
[10] Cf. S. E. Sheppard and R. C. Houck: J. Rheology, 1, 20 (1929).
[11] Cf. Wo. Ostwald's "Bodenkörperregel," Kolloid-Z., 41, 163 (1927). The polydisperse or polyhomologous condition indicates one reason for this.
[12] E. W. J. Mardles: J. Soc. Chem. Ind., 42, 127T (1923); Kolloid-Z., 49, 4 (1929).
[13] Cf. Brown and Bogin: Ind. Eng. Chem., 19, 969; J. G. Davidson and E. W. Reid: 977 (1927).
[14] Cf. Th. H. Durrans: "Solvents" p. 7. Davidson and Reid used 2.5 grams cellulose nitrate in 7.5 grams of solvent.
[15] E. W. J. Mardles: J. Soc. Chem. Ind., 42, 135T (1923).
[16] Cf. Mardles: loc. cit.; McBain, Harvey and Smith: J. Phys. Chem., 30, 312 (1926).
[17] Highfield: Trans. Faraday Soc., 21, 57 (1926).
[18] S. E. Sheppard, E. K. Carver and R. C. Houck: Colloid Symposium Monograph, 5, 243 (1927).
[19] Wo. Ostwald: Kolloid-Z., 29, 100 (1921); also M. Kröger: 45, 46 (1928).
[20] I. Sakurada: Kolloid-Z., 48, 277 (1929).

THE INFLUENCE OF ETHYLENE GLYCOL
UPON SOME REACTIONS*

BY L. MABEL YOUNG AND H. M. TRIMBLE

Ethylene glycol is known to act as a preservative in food preparations. Some direct studies have been made, too, upon its inhibiting action toward the growth of bacilli, molds and yeasts.[1] The question of its effect upon certain related reactions was taken up as a part of a series of studies with this interesting substance which are being carried out in this laboratory.

All experiments were performed at 30°C. The ordinary chemicals used were all of C.P. quality. Ethylene glycol was prepared by distilling prestone or dynamite grade glycol as previously described[2] and its purity was established by suitable tests. The urease used was a fresh preparation manufactured from Jack bean meal by the Arlington Chemical Company.

The invertase was a preparation "for analysis" from the Digestive Ferments Company. Fleischmann's yeast purchased upon the open market was used in the fermentation experiments. A preparation of yeast grown in the laboratory was used in a few of the experiments. All glassware was cleansed with cleaning solution, washed well with distilled water and dried in a hot air bath before use.

Effect of Ethylene Glycol upon Activity of Urease

A number of semi-quantitative experiments upon the decomposition of urea by urease showed that the rate is diminished by the addition of even small quantities of glycol, that this effect increases with increasing concentration of this substance, and that about 60 per cent by volume will almost stop the reaction. Altering the concentrations of urea and of urease within the limits imposed by experimental conditions, the concentration of glycol being held constant, did not greatly alter the relative rates. The results, however, were erratic, and the results of parallel experiments often showed poor agreement. It was found that the difficulties could be practically eliminated by working with solutions which were heavily buffered, though this imposed serious restrictions upon the range of concentrations which could be covered.

Buffer solutions were prepared for more accurate experiments by mixing 50 volumes of molar KH_2PO_4 with 9 volumes of molar K_2HPO_4. Five cc. of the buffer solution was pipetted into a 250 cc. Soxhlet flask and 1 cc. of glycol added. Three cc. of freshly prepared urea solution of the desired concentration were next added. The flask was then set in the thermostat

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[1] Fuller: Ind. Eng. Chem., **16**, 624 (1924).
[2] Trimble: Ind. Eng. Chem., **23**, 165 (1931).

TABLE I

The Decomposition of Urea by Urease

Part 1

Control	Reaction Mixture
0.03 grams urea	Same as control except 1.083
0.001 grams urease preparation	grams of glycol added and the
5 cc. buffer solution	whole made up to 10 cc.
Water to make a volume of 10 cc.	

Time Minutes	Control Per cent decomposed	Reaction Mixture Per cent decomposed	Relative Activity
20	16.75	5.00	.30
40	28.25	8.75	.31
60	37.00	11.50	.31
80	43.75	13.10	.30
100	48.50	14.00	.28
120	52.30	14.50	.28
		Average	.30

Part 2

Control	Reaction Mixture
0.06 grams urea	Same as control except 1.083
0.001 grams urease preparation	grams of glycol added and the
5 cc. buffer solution	whole made up to 10 cc.
Water to make a volume of 10 cc.	

Time Minutes	Control Per cent decomposed	Reaction Mixture Per cent decomposed	Relative Activity
20	7.30	2.77	.38
40	14.00	5.25	.38
60	18.60	6.80	.37
80	22.25	8.30	.37
100	25.60	9.00	.35
120	28.50	9.10	.32
		Average	.36

Part 3

Control	Reaction Mixture
0.12 grams urea	Same as control except 1.083
0.001 grams urease preparation	grams of glycol added and the
5 cc. buffer solution	whole made up to 10 cc.
Water to make a volume of 10 cc.	

Time Minutes	Control Per cent decomposed	Reaction Mixture Per cent decomposed	Relative Activity
20	7.25	2.75	.38
40	14.00	5.25	.38
60	20.30	7.20	.36
80	25.50	8.80	.35
100	29.25	9.80	.34
120	31.00	10.50	.34
150	31.50	11.00	.35
		Average	.36

weighed out in the form of pellets and gently macerated with such a quantity of distilled water as would give .001 gram in 1 cc. and brought to temperature. Then 1 cc. of this suspension was pipetted into each flask, the flask was shaken, stoppered, and returned to the thermostat; noting the time of starting the reaction. Control experiments were run in each set, using exactly the same quantities of the other materials, but substituting water for the glycol. The hydrogen ion concentration was followed by indicator methods in a number of cases. It was found to remain constant throughout at pH = 7.30.

At suitable intervals the reactions in successive flasks were stopped by adding 35 cc. of saturated Na_2CO_3 solution. The flasks were then placed in a hot water bath kept at a temperature just under the boiling point of water and, by passing air through the mixture for two hours the ammonia was driven over into an excess of 0.1134 normal H_2SO_4 to which had been added 50 cc. of distilled water. No trace of ammonia could be detected in the flasks after that period of aeration. Kjeldahl connecting bulbs were used in order to keep any spray from entering the bottles of acid. In order to find the amount of ammonia driven out of the reaction flasks the excess H_2SO_4 was then titrated with NaOH which had been standardized against standard HCl. Phenolphthalein was the indicator used. This method followed in general that of Rockwood and Husa.[3]

Repeated experiments were performed with solutions of three compositions, with their corresponding controls. All results for each of the sets were plotted, and the best curve drawn through the points. From these curves the per cents decomposed at intervals of 20 minutes were read. Experiments were not continued for longer times than two hours because of the danger of losing ammonia from the flasks through absorption by the rubber stoppers. The agreement was good, considering the difficulty of reproducing a biological material such as the enzyme here used. The data are presented in Table I. The fourth column headed "Relative Activity" is obtained by dividing the values of column 3 by the corresponding values of column 2. It serves as a measure of the inhibition brought about by added glycol. Obviously glycol present to the extent of 10% by volume reduces the activity of urease, under the conditions of the experiment, to approximately one-third the value which it has in an aqueous solution at the same concentration.

Effect of Ethylene Glycol upon Fermentation

The second reaction studied was the fermentation of sugars by Fleischmann's yeast. Secondary ammonium phosphate was used as additional nutrient material.

The apparatus used in studying the rate of fermentation is shown in Fig. 1. A stirrer projected into the flask through a mercury seal, so that no loss of gases was possible. The mixture was stirred at a constant rate throughout the entire course of the experiment. In one hole of the stopper in the side arm of the flask a manometer tube filled with water was placed. In the other hole of the stopper was an outlet tube at the end of which was a short length

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[3] J. Am. Chem. Soc., **45**, 2678 (1923).

of rubber tubing which could be opened or closed by a screw clamp. The reaction mixture of sugar, $(NH_4)_2HPO_4$, H_2SO_4, and ethylene glycol (or water) for a given experiment, 75 cc. in volume, was placed in the Soxhlet flask. There were 5 cc. of 1.083 N. H_2SO_4 in each 75 cc. of the solution. One cake of Fleischmann's yeast was put in suspension with 150 cc. of water
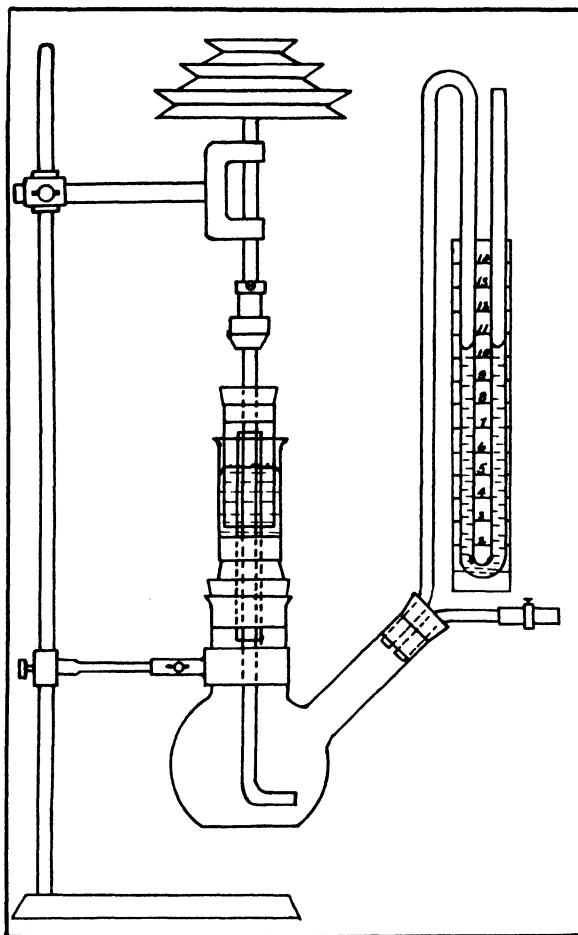
Fig. 1
Reaction Apparatus for Fermentation

and brought to 30°C. 25 cc. of the yeast suspension was then added through the side arm, the outlet tube tightly closed, and after five minutes the increase of pressure set up by the evolution of CO_2 was measured by reading the displacement of the column of liquid in the manometer on a millimeter scale. The outlet tube was then quickly opened and the pressure in the two arms of and allowed to come to temperature. The urease preparation was now the tube equalized. The tube was then closed and the pressure again allowed to build up. This releasing of the pressure never consumed more than 15

seconds at most. Yeast from the same cake was always used for an experiment with glycol present and for its control.

In order to find the quantity of carbon dioxide evolved during the fermentation it was assumed that the perfect gas law holds. Since CO_2 is not a perfect gas, some error is involved in so considering it, but the error is, we believe, within the limits of the experimental error of the work itself. We have, then:

$$p_1v = n_1RT \text{ and } p_2v = n_2RT$$

$$\text{then } (n_2 - n_1) = \frac{p_2v}{RT} - \frac{p_1v}{RT}$$

$$\text{and } (n_2 - n_1) = \frac{v}{RT} \Delta p$$

where $(n_2 - n_1)$ is the number of mols of CO_2 liberated in unit time, R is the gas constant expressed in cc. millimeters of mercury, v is the volume of the space above the solution in the flask, T is the absolute temperature, and Δp is the increase in pressure per unit of time, expressed in millimeters of mercury. From the numbers of mols so obtained the volumes of carbon dioxide evolved for the various times, reduced to standard conditions, were calculated. A summation of these quantities, making allowance for the periods during which the pressure was being released, gave the quantities of gas liberated at the various times.

Readings of the manometer were taken every five minutes, but for convenience the tables were made using twenty-five minute intervals Table II shows the results obtained for representative experiments. All curves for both sucrose and glucose were found to follow the same general form. While these results could not be exactly reproduced, due to the variable nature of yeast, yet other experiments gave results closely parallel to these.

<div align="center">

TABLE II

The Fermentation of Glucose with Fleischmann's Yeast

</div>

The reaction mixtures in each of the following experiments were made up using the quantities of the reacting substances indicated. In the control mixtures water was substituted in each case for equal volumes of glycol. The average results of the experiments are given.

<div align="center">

Part 1

</div>

0.75 grams glucose   25 cc. yeast suspension
0.50 grams $(NH_4)_2HPO_4$ % glycol below indicated, by volume
5 cc. 1.083 N. H_2SO_4 Water to make a volume of 100 cc.

Control			Reaction Mixture		
Per cent glycol	Time	Vol. CO_2 evolved	Per cent glycol	Vol. CO_2 evolved	Relative activity
0.00	25 min.	13.98 cc.	20	4.29 cc.	.31
	50 "	27.98 "		9.78 "	.35
	75 "	40.27 "		14.39 "	.36
	100 "	53.47 "		18.42 "	.35
	125 "	62.26 "		22.15 "	.36

<div align="center">TABLE II (continued)</div>

<div align="center">Part 2</div>

Per cent glycol	Time	Vol. CO_2 evolved	Per cent glycol	Vol. CO_2 evolved	Relative activity
0.00	25 min.	9.42 cc.	50	1.29 cc.	.14
	50 "	20.50 "		2.05 "	.10
	75 "	30.79 "		2.54 "	.082
	100 "	40.31 "		2.96 "	.074
	125 "	46.97 "		3.22 "	.069

The Fermentation of Sucrose with Fleischmann's Yeast

The same concentrations of the reacting substances were used as in the glucose experiments, the sucrose being substituted for an equal weight of glucose.

<div align="center">Part 3</div>

Per cent glycol	Control Time	Vol. CO_2 evolved	Reaction Mixture Per cent glycol	Vol. CO_2 evolved	Relative activity
0.00	25 min.	5.68 cc.	20	3.43 cc.	.60
	50 "	16.40 "		9.98 "	.60
	75 "	25.88 "		14.30 "	.55
	100 "	34.56 "		17.69 "	.51
	125 "	41.73 "		20.38 "	.49

<div align="center">Part 4</div>

Per cent glycol	Time	Vol. CO_2 evolved	Per cent glycol	Vol. CO_2 evolved	Relative activity
0.00	25 min.	5.62 cc.	50	1.40 cc.	.25
	50 "	13.36 "		1.77 "	.13
	75 "	20.79 "		1.94 "	.093
	100 "	27.25 "		2.04 "	.075
	125 "	32.84 "		2.04 "	.062

<div align="center">Part 5</div>

			75	0.00 cc.	
				0.00 "	
				0.16 "	
				0.16 "	
				0.16 "	

As shown by the last columns of the table, part 1, the activity of yeast in bringing about fermentation of glucose is reduced to approximately 1/3 its value by addition of 20% glycol by volume. With 50% glycol present, (part 2) the activity is reduced to about 1/7 of its value in the absence of glycol and this inhibition increases with time until, after 125 minutes, it has nearly doubled.

In the fermentation of sucrose (part 3) 20% of glycol by volume reduces the activity of the yeast to about 2/3 of the value which it has in the aqueous solution, at the start. After 125 minutes the activity has been reduced to about half its normal value. With 50% glycol (part 4) the inhibition approaches that found with the same relative amount when fermenting glucose. With 75% glycol (part 5) inhibition of fermentation is complete within the limits of experimental error.

Effect of Ethylene Glycol upon Inversion of Sucrose

Because of its accuracy and convenience the polariscope was used to determine the rate of inversion of sucrose. The rate of inversion of sucrose with invertase was studied, first without and then with added glycol. The polariscope tubes were of the water jacketed form, and were supplied with water from a thermostat at 30°. They were washed first with water, then with alcohol, and finally with distilled water, then rinsed several times with the solution whose rate of inversion was to be studied.

One hundred cc. of the reaction mixture in each case was brought to 30°C. in the water bath. The sucrose solution had been made acid to litmus with acetic acid in order to establish a suitable pH. This is not highly important, however, for it has been found that for the action of invertase the pH may vary over quite a large range without detrimental effects. After the solution had been brought to temperature 5 cc. of invertase solution, also at 30°C. was added and the solution introduced into the polariscope tubes. Measurements of the angle of rotation were made at suitable intervals for 90 to 774 minutes in various experiments, depending upon the velocity of the reaction in each case. A sodium fed flame was used as light source.

It is most convenient to express velocities of inversion in terms of K, the reaction rate at zero time, or the velocity constant.

For a reaction of the first order, according to which this reaction is most readily formulated, we have:

$$(1) \quad K = -\frac{1}{t}\log_e \frac{A + A_o}{A_t + A_o}$$

or

$$(2) \quad K = \frac{1}{t}\log_e (A_t + A_o) - \log_e (A + A_o)$$

where A, A_t and A_o are, respectively, the specific rotations at zero time, at time t and at complete inversion. Specific rotations were calculated by means of the equation $(A)_D^t = \frac{a\ v}{l\ g}$, where $(A)_D^t$ is the specific rotation at time t, a is the angle of rotation as measured, g is the number of grams of sucrose dissolved in v cc. of water, and l is the length of the polarimeter tube in decimeters. The equation giving the specific rotation of invert sugar is $(A)_D^t = -(27.90 - 0.32\ t)$[4] from which we find that the specific rotation at

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[4] Woodman: "Food Analysis," 250 (1924).

total inversion at $30°$, A_o is -18.30. This value was also found by direct measurement. Obviously the term $\log_e (A + A_o)$ in equation (2) is constant. If, then, $\log_e (A_t + A_o)$ be plotted as ordinate against t as abscissa, we have a straight line of which K, the velocity constant is the slope. In finding K the point formula for a straight line was employed. The difference of $\log_e (A_t - A_o)$ for two different times was divided by the difference of the times. The average of all such approximate values of K for a given experiment was taken as its characteristic velocity constant. The plot of values of $\log_e (A_t + A_o)$ against t always approximated closely a straight line. The velocity constants for any set of curves showed good agreement. The average of all the values for a given set was taken as the representative velocity constant.
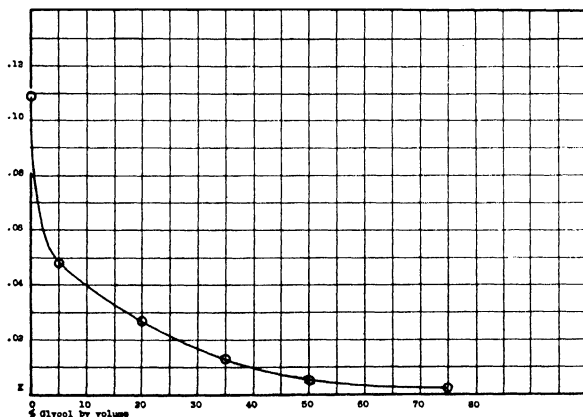
FIG. 2

Inversion of Sucrose by Invertase in presence of Glycol

TABLE III

The Inversion of 3 Per Cent Sucrose with Invertase

Per cent glycol by volume	K per minute
0.00	−0.109
5.00	−0.048
20.00	−0.027
35.00	−0.013
50.00	−0.005
75.00	−0.002

Table III gives the average velocity constants for the inversion of solutions containing 3 per cent sucrose by weight together with a little acetic acid, as catalyzed by invertase, for various quantities of added ethylene glycol. The results are also set forth in Fig. 2. The degree of inhibition for various per cents of added glycol, by volume, will be clear from this curve. Six separate experiments were run for each concentration of glycol.

Turning, now, from reactions catalyzed by enzymes we studied the effect of added glycol upon the rates of inversion of sucrose in the presence of sulfuric and hydrochloric acids. All solutions contained 3% by weight of sugar. Solutions of sucrose and of acid were prepared in such volumes as when mixed would give 100 cc. of solution of the concentrations desired. They were separately brought to temperature, mixed and immediately introduced into the polariscope tubes. Four experiments were run for each con-
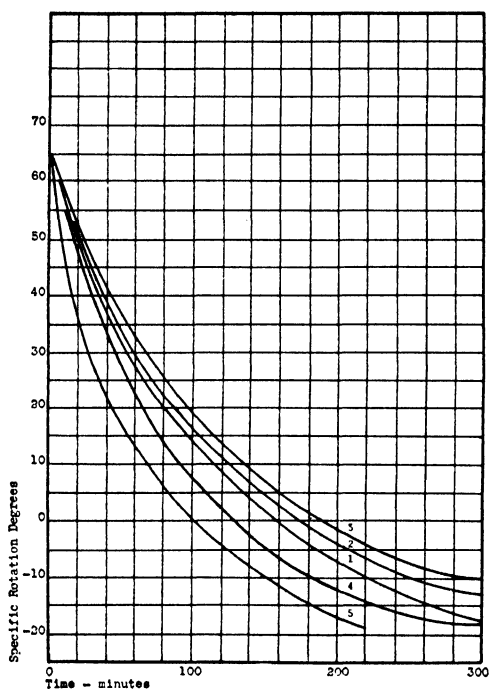
FIG. 3

Inversion of Sucrose catalyzed by 0.50 N HCl

1. No glycol K = −0.0103
2. 5 per cent glycol K = −0.0090
3. 20 per cent glycol K = −0.0080
4. 35 per cent glycol K = −0.0120
5. 50 per cent glycol K = −0.0168

centration of glycol with normal and half normal sulfuric and hydrochloric acids, two each for .2 normal sulfuric and hydrochloric acids.

Space will not permit the presentation of all the data, but those for the rate of inversion catalyzed by 0.50 normal HCl may be taken as typical. They are presented graphically in Fig. 3 and the corresponding velocity constants, taken from Table IV, are given.

The data for all these experiments are presented in Table IV, where the velocity constants for various concentrations of glycol and acid are given. They are represented graphically in Fig. 4, where K is plotted against per cent of glycol.
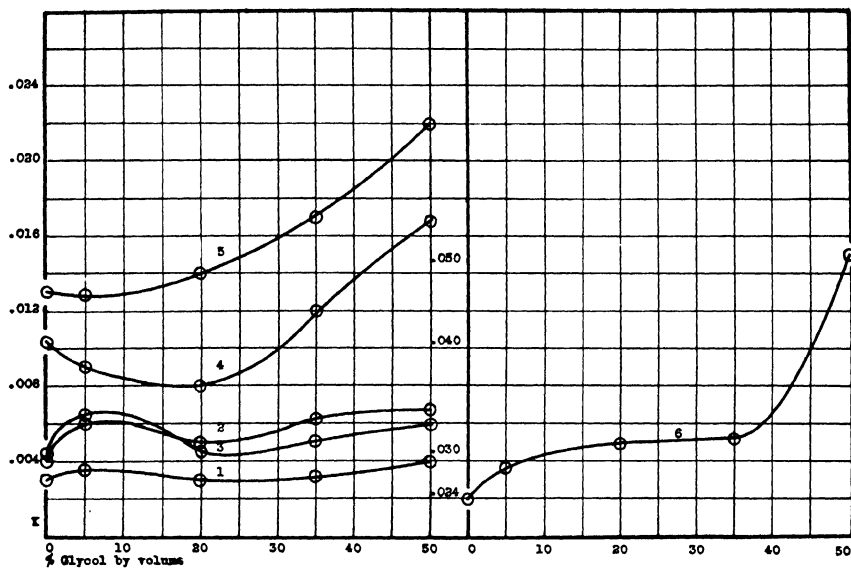
FIG. 4

Inversion of Sucrose by Acids in presence of Glycol

1. 0.2 N H_2SO_4	4. 0.50 N HCl
2. 0.2 N HCl	5. 1.00 N H_2SO_4
3. 0.4928 N H_2SO_4	6. 1.00 N HCl

TABLE IV

The Inversion of 3 Per Cent Sucrose Catalyzed by Acid

Per cent glycol by volume	0.20 N. H_2SO_4 K per min.	0.20 N. HCl K per min.
0	−0.0030	−0.0040
5	−0.0036	−0.0060
20	−0.0030	−0.0050
35	−0.0032	−0.0063
50	−0.0040	−0.0068

Per cent glycol by volume	0.4928 N. H_2SO_4 K per minute	0.50 N. HCl K per min.
0	−0.0042	−0.0103
5	−0.0065	−0.0090
20	−0.0045	−0.0080
35	−0.0051	−0.0120
50	−0.0060	−0.0168

Per cent glycol by volume	1.00 N. H_2SO_4 K per min.	1.00 N. HCl K per min.
0	−0.0130	−0.0240
5	−0.0129	−0.0267
20	−0.0140	−0.0300
35	−0.0170	−0.0310
50	−0.0220	−0.0500

The strange nature of the results will be apparent from the nature of the curves. When our first experiments revealed these peculiarities we returned and repeated them with great care, making every effort to remove all sources of error. We feel great confidence in the essential correctness of our results. In confirmation of their essential correctness we have the work of Ganguli and Malkani.[5] In an article published since this work was completed they have set forth the results of a study of the catalysis of the inversion of sucrose by o.1 normal HCl as modified by added ethylene glycol. In general their curves resemble those found by us in these experiments.

We are quite at a loss to account for the effect of ethylene glycol upon the rate of inversion of sugar in the presence of acids. One of us has proved that, in concentrations as great as 5 mols per liter, it does not react appreciably with HCl or H_2SO_4. The concentrations of acid were as high as 3 mols per liter and the time as long in some experiments as five weeks. The esterification with acetic acid, on the other hand proceeded regularly and normally. In another study made in this laboratory, whose results are soon to be published, no sign of esterification was found with either HCl or H_2SO_4. The acid concentration ran as high as molar with as much as 10 mols of glycol present per liter. The hydrogen electrode method was used in making the measurements. Determinations of hydrogen ion concentrations using both the hydrogen electrode and the quinhydrone electrode have failed to reveal any such alteration of hydrogen ion concentration with concentration of sucrose or glycol as would be required to explain these irregularities. Compound formation between sucrose and glycol, it seems, would show more regular alterations with increasing concentrations of glycol, if this is the factor which is responsible.

It has been found by Scatchard[6] and others that the hydrogen ion concentration of a solution changes as inversion proceeds with HCl as catalyst. The change is small, however, not more than 10 millivolts at the most. Scatchard, in fact, is inclined to attribute it to an alteration in boundary potential as shown by the potential of the cell used. Pennycuick[7] states that the hydrogen ion activity increases regularly during inversion by 1 to 3 per cent, according to the strength of the acid. It should be noted that both these workers inverted very much more sucrose in their experiments than we did. We, too, have found indications of a slight increase in hydrogen ion activity as the inversion of sucrose progresses, using the quinhydrone electrode technique. The course of inversion in these solutions, however, did not in any sense parallel this change.

It does not seem possible that any change in hydrogen ion concentration which is possible in these solutions could have produced the irregularities which we have found. Neither does it seem reasonable to attribute the irregularities to alterations in the degree of hydrolysis of the sucrose or alterations in the viscosity of the solutions.

[5] J. Phys. Chem., **35**, 2368 (1931).

[6] J. Am. Chem. Soc., **48**, 2026 (1926).

[7] J. Am. Chem. Soc., **48**, 6 (1926).

Probably explanation of such results as those which we have found in all the cases which we have studied must wait until a better understanding of the nature of the combination between a catalyst and its substrate has been gained.

Summary

The effect of ethylene glycol upon the rate of destruction of urea by urease, upon the rate of fermentation of sugars by yeast, upon the rate of inversion of sucrose by invertase and upon the rate of inversion of sucrose by acids has been studied.   It is found that enzyme activity is inhibited by the addition of ethylene glycol, and this inhibition is nearly complete if as much as 75 per cent by volume be added.   The inversion of sucrose with acids as catalysts is sometimes promoted, sometimes retarded by the addition of glycol.

November 24, 1931.

THE PHYSICAL PROPERTIES OF THE TERNARY SYSTEM ACETONE—n-BUTYL ALCOHOL—WATER*

BY R. C. ERNST, E. E. LITKENHOUS, AND J. W. SPANYER, JR.

The density, contraction in volume, and limits of miscibility of the system acetone—n-butyl alcohol—water have been investigated by Reilly and Ralph.[1]

The limits of miscibility were also studied by Jones.[2]

In this investigation a further study is made of this system and the following properties determined: density, viscosity, surface tension, refractive index, and boiling points.

Experimental

Materials. The acetone used was of C.P. grade and was treated repeatedly with powdered sodium hydroxide. It was further purified by fractional distillation and drying over calcium chloride.[3] Normal butyl alcohol of C.P. grade was treated with sodium acid sulfite, refluxed with lime, fractionally distilled, and finally dried over metallic calcium.[4]

All materials were repeatedly distilled until chemical tests showed no traces of aldehydes, acids, or esters after which a final distillation was made. Water was treated successively with potassium dichromate and barium hydroxide and then distilled.

The physical constants of these materials with the results of other experimenters are given in Table I.

Preparation of Samples. The samples were prepared on a weight percent basis in increments of ten percent. The densities of the pure substances were first determined and volumes equivalent to the weights desired were measured by means of a standardized burette.
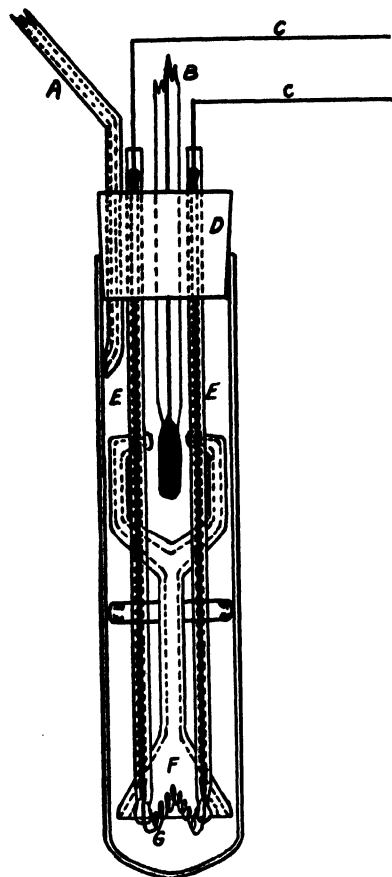
Fig. 1
Boiling Point Apparatus
Key: A. Condenser. B. Calibrated Thermometer
C. Electric Wires to Source
D. Stopper
E. Glass Contact Tubes filled with Mercury
F. Percolator
G. Chromium-Nickel Heating Coil

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[1] Sci. Proc. Roy. Dublin Soc., 15, 597-608 (1919).
[2] J. Chem. Soc., 1929, 799-813.
[3] Kahlbaum, Clarke, Robinson and Smith: J. Chem. Soc., 1927, 2244.
[4] Brunel, Crenshaw, and Tobin: J. Am. Chem. Soc., 43, 561 (1921).

TABLE I

Physical Constants of Purified Products

	Density D_{25}^{25}	Viscosity n_{25}	Surface Tension S_{25}	Refractive Index N_D^{25}	Boiling Points °C
Acetone	.7878*	.003439*	22.996*	1.3570*	56.24*
	.7882[5]	.00316[6]	22.17[5]	1.35545[7]	56.1 − .2[8]
	.7882[9]	.0029530[10]	22.56[11]	1.3569[12]	56.3[2]
Butyl	.8080*	.002465*	24.204*	1.3981*	117.69*
Alcohol	.8080[4]	.02438[13]	24.10[14]	1.3974[4]	117.71[4]
	.8061[15]		24.23[16]	1.39790[12]	117.6[17]
				1.39747[17]	
Water	.99707	.00893	71.97	1.3330*	100.0
	.99707[18]	.0089481[19]	71.86[5]	1.3232[7]	
		.0089262[20]		1.3325[21]	

The composition of the resulting sixty-six samples are given in Table II both by weight percent and by mol fraction.

Apparatus. The determination of the density, viscosity, surface tension, and refractive index were carried out at a constant temperature of 25 ± .05° C. A constant temperature bath, thermostatically controlled, was used with a rotary pump supplying water to the refractometer. All samples were kept in stoppered bottles in the constant temperature bath for twenty-four hours before using.

* Authors' experimental values.
[5] Morgan and Scarlett: J. Am. Chem. Soc., **39**, 2275 (1917).
[6] Baker: J. Chem. Soc., **103**, 1653 (1913).
[7] Glazunov: Annales de l'Institut Poly. Pierre-le-Grand, Petrograd, **21**, 291 (1914).
[8] Shipsey and Werner: J. Chem. Soc., **103**, 1255 (1913).
[9] Price: J. Chem. Soc., **65**, 1116 (1919).
[10] Bramley: J. Chem. Soc., **109**, 10 (1916).
[11] Reynard and Guye: J. Chim. phys., **5**, 81 (1907).
[12] Peacock: J. Chem. Soc., **107**, 1547 (1915).
[13] Thorpe and Rodger: Phil. Trans., **185**, 397 (1895).
[14] Morgan and Stone: J. Am. Chem. Soc., **43**, 566 (1921).
[15] Herz and Schuftan: Z. physik. Chem., **101**, 269 (1922).
[16] Richards and Mathews: J. Am. Chem. Soc., **30**, 88 (1908).
[17] Kahlbaum: Z. physik. Chem., **46**, 628-646 (1898).
[18] Chappuis: Bureau International des Poids et Mesures, Travaux et Memoires, **13**, (1907).
[19] Bingham and White: Z. Physik., **80**, 670 (1912).
[20] Hosking: Proc. Roy. Soc. N. S. Wales, **43**, 37 (1909).
[21] Quincke: Ann. Physik, **44**, 774 (1891).

TABLE II

Composition of Samples

Sample Number	Wt. Pct. Acetone	Wt. Pct. Butyl Alcohol	Wt. Pct. Water	Mol. Fr. Acetone	Mol. Fr. Butyl Alcohol	Mol. Fr. Water
1	—	100	—	—	1.000	—
2	—	—	100	—	—	1.000
3	100	—	—	1.000	—	—
4	—	10	90	—	.026	.974
5	—	20	80	—	.057	.943
6	—	30	70	—	.094	.906
7	—	40	60	—	.139	.861
8	—	50	50	—	.196	.804
9	—	60	40	—	.267	.733
10	—	70	30	—	.362	.638
11	—	80	20	—	.494	.506
12	—	90	10	—	.687	.313
13	90	—	10	.736	—	.264
14	80	—	20	.554	—	.446
15	70	—	30	.420	—	.580
16	60	—	40	.318	—	.682
17	50	—	50	.237	—	.763
18	40	—	60	.171	—	.829
19	30	—	70	.118	—	.882
20	20	—	80	.070	—	.930
21	10	—	90	.033	—	.967
22	10	90	—	.124	.876	—
23	20	80	—	.242	.758	—
24	30	70	—	.354	.646	—
25	40	60	—	.460	.540	—
26	50	50	—	.561	.439	—
27	60	40	—	.657	.343	—
28	70	30	—	.749	.251	—
29	80	20	—	.836	.164	—
30	90	10	—	.920	.080	—
31	80	10	10	.666	.065	.269
32	70	10	20	.492	.055	.453
33	60	10	30	.365	.047	.588
34	50	10	40	.268	.042	.690
35	40	10	50	.192	.037	.771
36	30	10	60	.130	.034	.836
37	20	10	70	.079	.031	.890
38	10	10	80	.036	.029	.935
39	70	20	10	.594	.133	.273
40	60	20	20	.428	.112	.460

TABLE II (Continued)

Composition of Samples

Sample Number	Wt. Pct. Acetone	Wt. Pct. Butyl Alcohol	Wt. Pct. Water	Mol. Fr. Acetone	Mol. Fr. Butyl Alcohol	Mol. Fr. Water
41	50	20	30	.308	.097	.595
42	40	20	40	.216	.085	.699
43	30	20	50	.145	.076	.779
44	20	20	60	.087	.068	.845
45	10	20	70	.040	.062	.898
46	60	30	10	.518	.203	.279
47	50	30	20	.363	.170	.467
48	40	30	30	.250	.147	.603
49	30	30	40	.164	.129	.707
50	20	30	50	.098	.115	.787
51	10	30	60	.044	.104	.852
52	50	40	10	.438	.278	.284
53	40	40	20	.294	.231	.475
54	30	40	30	.189	.198	.613
55	20	40	40	.110	.174	.716
56	10	40	50	.049	.157	.794
57	40	50	10	.359	.352	.289
58	30	50	20	.222	.293	.485
59	20	50	30	.128	.252	.620
60	10	50	40	.056	.220	.724
61	30	60	10	.275	.430	.295
62	20	60	20	.152	.358	.490
63	10	60	30	.067	.305	.628
64	20	70	10	.187	.512	.301
65	10	70	20	.077	.425	.498
66	10	80	10	.095	.598	.307

Relative densities were determined using a Geissler pycnometer[22] of fifty cc. capacity. The pycnometer with the sample was placed in a cell in the constant temperature bath for one hour before weighings were made.

A modified Ostwald-Poiseuille viscosimeter[23] was used for determining viscosity. The viscosimeter was immersed in the constant temperature bath and readings made by means of a telescope with suitable illumination. Constant volume was used in all determinations, and a stop watch with an accuracy of one-fifth of a second was employed.

The surface tension was determined by means of a capillary tube[24] immersed in the constant temperature bath.

[22] Central Scientific Company Catalogue, C-227, 118 (1930).

[23] Wiss.: Abhandl. Phys. Tech. Reichsanstalt, 4, 241 (1904).

[24] Findlay: "Practical Physical Chemistry," 91 (1925).

The Abbe refractometer[25] was used for the determination of refractive indices. The prisms were maintained at constant temperature by water from the constant-temperature bath.

For the determination of the boiling points a modification of the Cottrell apparatus[26] was constructed as shown in Fig. 1.

In this apparatus the liquid was kept in equilibrium with the vapor phase and the composition kept constant by refluxing the vapor back into
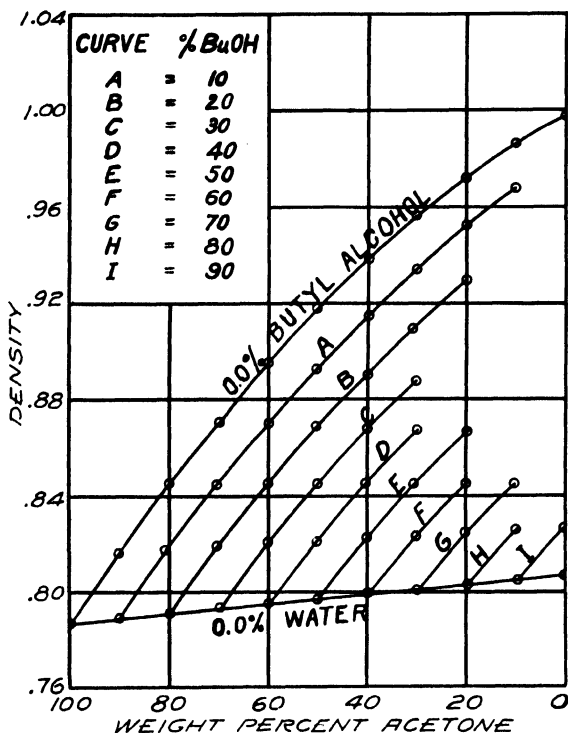
FIG. 2
Relative Density Acetone–n-Butyl Alcohol–Water at 25± .05°C

the solution. Superheating was prevented by employing internal electric heating and continually washing the bulb of a calibrated thermometer with the boiling liquid by means of a small glass percolator. Constant pressure was maintained in the system by means of an air pump connected in series with a large air reservoir, manometer, and condenser. The thermometer used was a −20 to 210° C mercury thermometer graduated in fifths of a degree. It was calibrated by comparison with a U. S. Bureau of Standards calibrated thermometer and by determining the freezing points and boiling points of pure metals and compounds.

Discussion

The results of the experimental work are summarized in Table III.

[25] Daniels, Mathews, and Williams: "Experimental Physical Chemistry," 323 (1930).
[26] Cottrell: J. Am. Chem. Soc., 41, 721 (1919).

TABLE III

Physical Properties

Sample Number	Density D_{25}^{25}	Viscosity n_{25}	Surface Tension S_{25}	Refractive Index N_D^{25}	Boiling Point B.P._760
1	.8080	.024850	24.20	1.3981	117.69
2	.99707	.008930	71.97	1.3330	100.00
3	.7878	.003439	22.99	1.3570	56.24
4*	—	—	—	—	92.98
5*	—	—	—	—	92.98
6*	—	—	—	—	93.04
7*	—	—	—	—	93.09
8*	—	—	—	—	93.14
9*	—	—	—	—	93.16
10*	—	—	—	—	93.19
11*	—	—	—	—	93.40
12	.8280	.025980	24.90	1.3938	96.45
13	.8172	.004509	25.56	1.3616	58.01
14	.8462	.006261	26.77	1.3638	59.68
15	.8717	.008365	27.72	1.3645	60.79
16	.8960	.010830	29.28	1.3635	61.60
17	.9191	.012400	31.60	1.3609	62.71
18	.9397	.013250	33.91	1.3579	64.42
19	.9570	.013360	37.00	1.3529	67.24
20	.9721	.012900	40.93	1.3470	70.09
21	.9861	.011210	47.27	1.3401	78.19
22	.8055	.016500	24.14	1.3934	101.35
23	.8036	.011640	24.17	1.3891	88.49
24	.8015	.008875	24.10	1.3850	80.00
25	.7994	.007108	24.04	1.3808	74.21
26	.7974	.005919	23.98	1.3770	70.03
27	.7953	.005089	23.92	1.3727	66.34
28	.7932	.004285	23.86	1.3686	63.32
29	.7913	.004014	23.80	1.3645	60.90
30	.7894	.003651	23.74	1.3607	58.68
31	.8196	.005058	25.35	1.3644	60.28
32	.8462	.007148	26.03	1.3663	61.62
33	.8716	.009800	27.56	1.3668	62.81
34	.8948	.011875	28.45	1.3654	64.42
35	.9160	.014070	29.12	1.3634	66.85
36	.9355	.014930	28.62	1.3595	69.88
37	.9534	.015135	27.86	1.3548	74.42
38	.9694	.014430	26.31	1.3491	79.89
39	.8204	.005655	24.80	1.3684	62.44
40	.8466	.008242	26.04	1.3705	64.22
41	.8708	.011080	26.64	1.3698	65.96

TABLE III (Continued)

Physical Properties

Sample Number	Density D_{25}^{25}	Viscosity n_{25}	Surface Tension S_{25}	Refractive Index N_D^{25}	Boiling Point B.P.$_{760}$
42	.8928	.013830	27.31	1.3682	68.77
43	.9129	.016350	26.67	1.3654	72.10
44	.9314	.017960	26.09	1.3618	76.56
45 *	—	—	—	—	84.05
46	.8215	.006744	25.12	1.3723	65.23
47	.8475	.009617	25.92	1.3732	67.00
48	.8695	.012865	26.15	1.3729	69.90
49	.8905	.016300	26.01	1.3710	73.33
50	.9092	.019570	25.85	1.3677	78.11
51 *	—	—	—	—	84.28
52	.8230	.007990	25.17	1.3756	68.16
53	.8471	.011515	25.47	1.3767	71.00
54	.8685	.015225	25.82	1.3757	75.64
55	.8879	.019360	25.54	1.3732	78.89
56 *	—	—	—	—	84.86
57	.8239	.009522	24.92	1.3794	71.71
58	.8473	.013980	25.48	1.3796	75.35
59	.8675	.018635	25.17	1.3784	79.90
60 *	—	—	—	—	84.97
61	.8258	.012000	25.23	1.3830	75.40
62	.8468	.017180	25.05	1.3830	80.31
63 *	—	—	—	—	85.25
64	.8260	.015090	24.56	1.3868	80.72
65	.8464	.021550	24.74	1.3862	86.30
66	.8269	.018920	24.16	1.3903	87.91

* Immiscible samples.

From these data both binoidal and triangular diagrams were drawn for each property. The binoidal curves are prepared so that the abscissae read the percent acetone while the ordinates read the particular property under consideration. The curves of constant property in the triangular diagrams were prepared from the binoidal curves, while the miscibility curve was taken from previous investigators.[27]

Density. Relative densities of all mixtures of the binary system acetone-butyl alcohol (Fig. 2) are intermediate between that of the pure substances. The curve for this property indicates that mixing is accompanied by a slight increase in volume. The densities for mixtures of acetone and water increase from acetone to water. The curve is not quite a straight line indicating that mixing is accompanied by a slight decrease in volume. When all three com-

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[27] Jones: J. Chem. Soc., **1929**, 799-813.
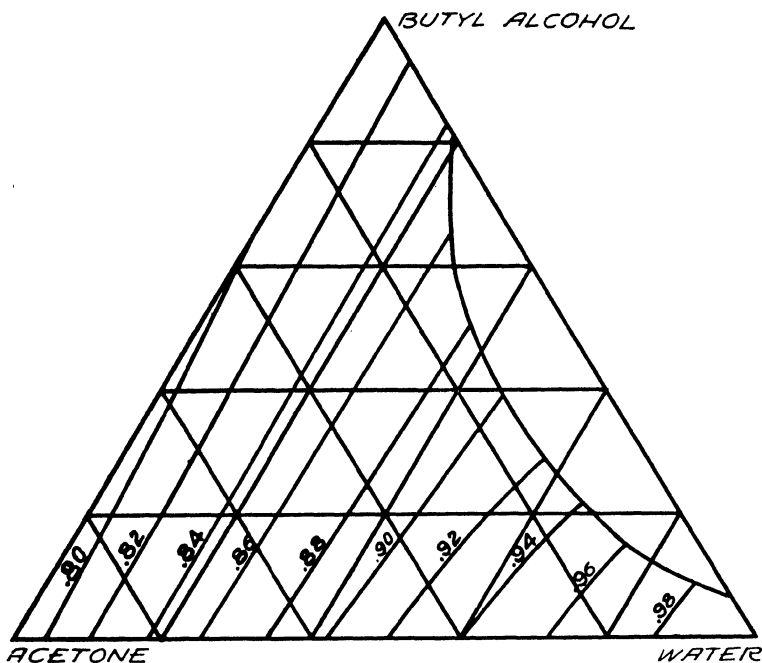
FIG. 3

Relative Density Acetone–n-Butyl Alcohol–Water at 25± .05°C
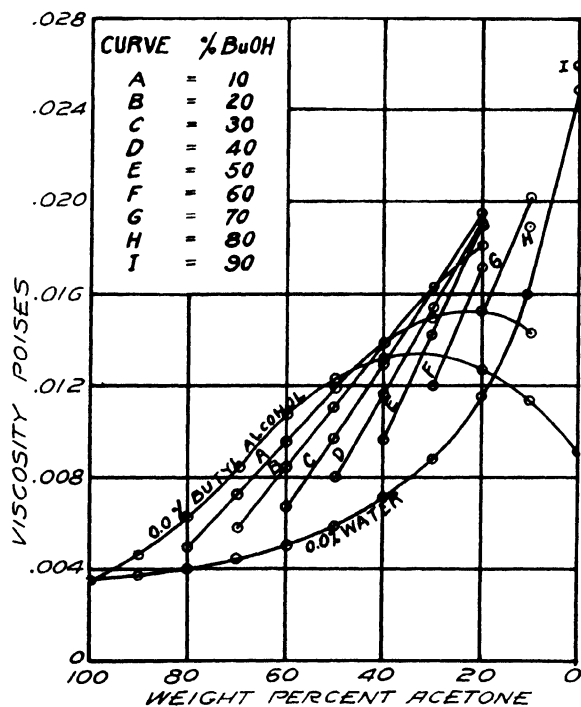
FIG. 4
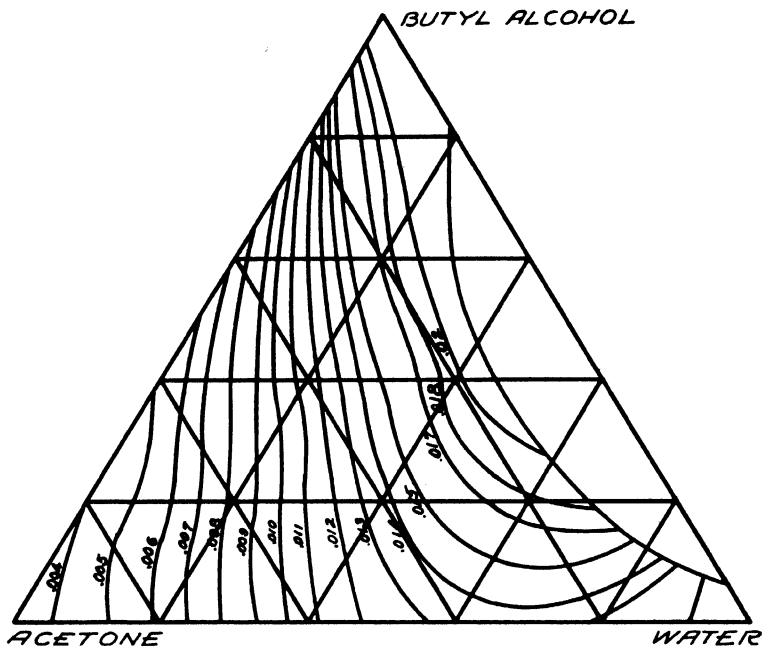
FIG. 5
Viscosity Acetone–n-Butyl Alcohol–Water at 25 ± .05°C
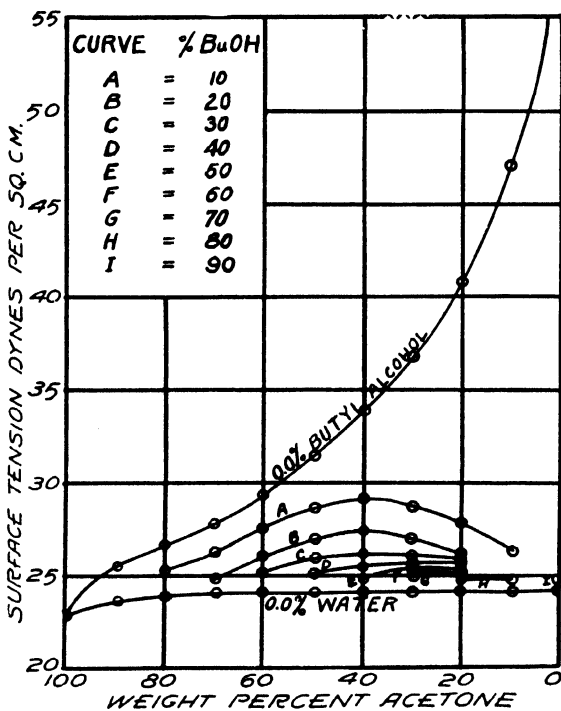
FIG. 6
Surface Tension Acetone–n-Butyl Alcohol–Water at 25 ± .05°C
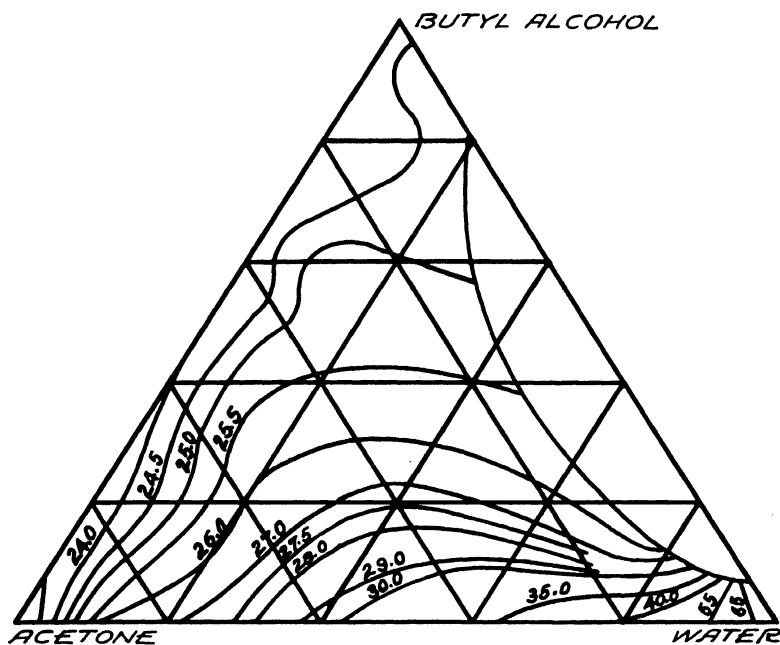
FIG. 7

Surface Tension Acetone–n–Butyl Alcohol–Water at $25 \pm .05°C$
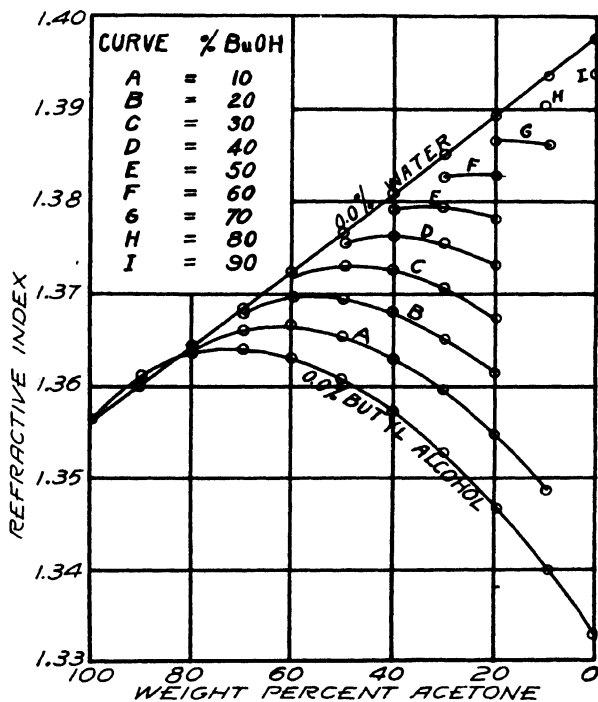
FIG. 8

Refractive Index Acetone–n–Butyl Alcohol–Water at $25 \pm .05°C$
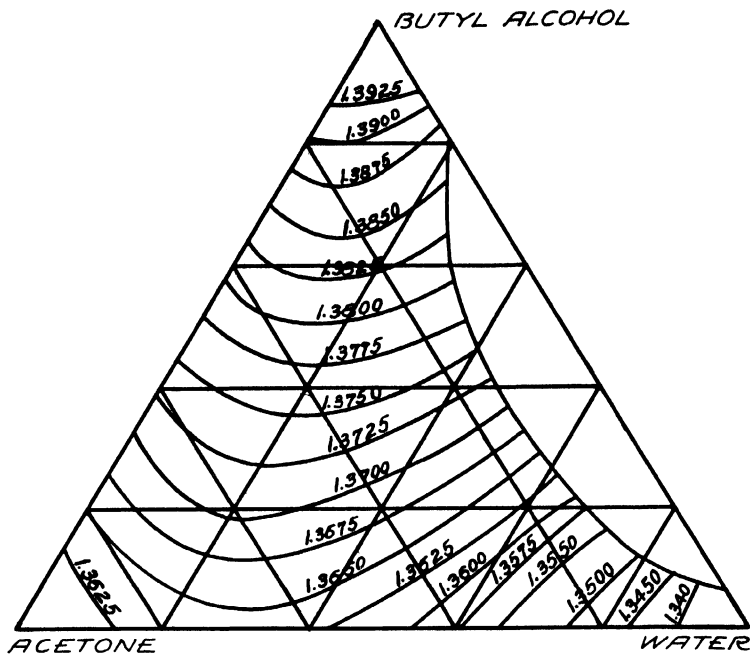
FIG. 9

Refractive Index Acetone–n-Butyl Alcohol–Water at 25 ± .05°C
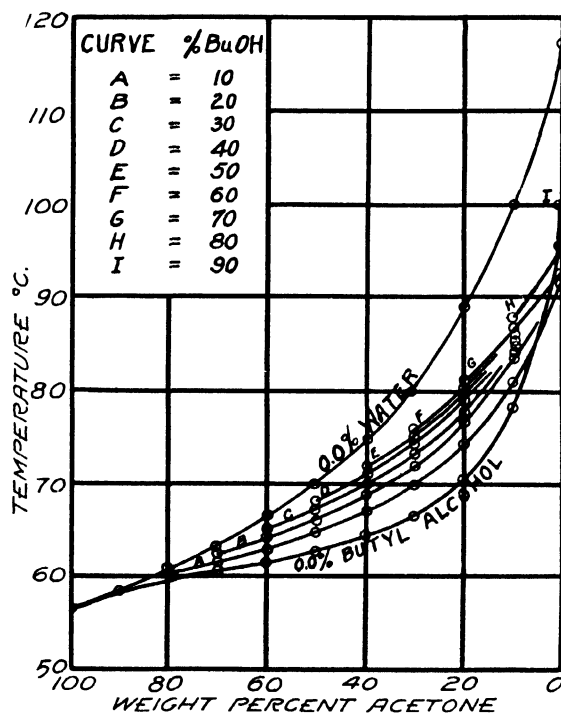
FIG. 10

Boiling Point Acetone–n-Butyl Alcohol–Water

ponents of the system acetone–n-butyl alcohol–water are present, the binoidal curves for constant percent butyl alcohol with the acetone and water as variables lie practically parallel to the acetone-water line. The constant density lines on the triangular diagram (Fig. 3) are practically parallel to the weight percent acetone lines. The density line 0.8400 is a straight line with the lines on either side becoming slightly concave outward. This is to be expected from the fact that the acetone and butyl alcohol binoidal curves show a slight increase in volume while the acetone-water binoidal curves show a slight decrease in volume.
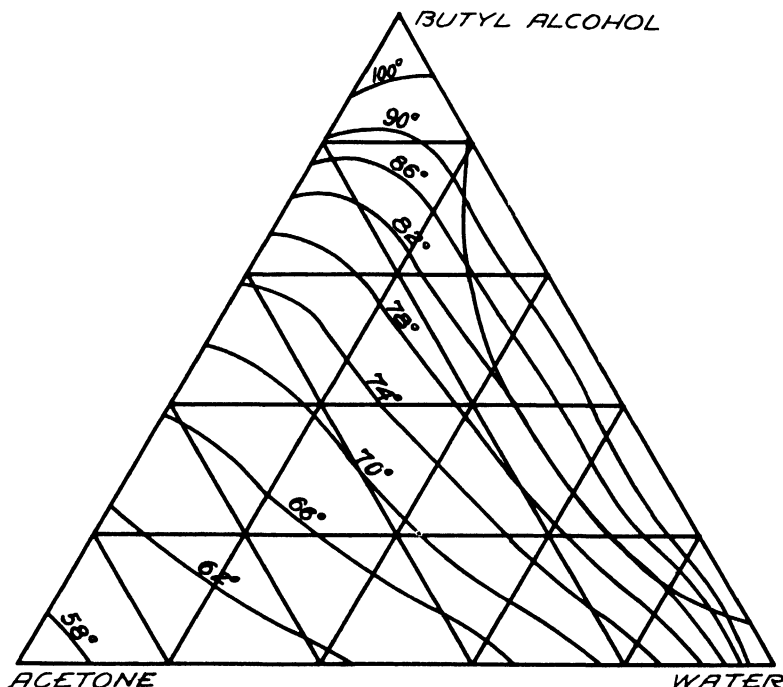
FIG. 11
Boiling Point Acetone–n-Butyl Alcohol–Water at 25± .05°C

Viscosity. The acetone-butyl alcohol viscosity line of the binary system (Fig. 4) increases from acetone to butyl alcohol giving a smooth curve with neither a maximum nor a minimum. The acetone-water curve passes through a maximum viscosity between forty and fifty percent acetone. This would be expected because of the decrease in volume upon mixing the two components. In the viscosity curve for the ternary system, the effect of the water in creating a maximum is gradually diminished as the percent of butyl alcohol is increased. In the triangular diagram (Fig. 5), showing constant viscosity lines, the influence of the water in creating a maximum is shown by the convex downward curvature of the lines as they approach pure water.

Surface Tension. The surface tension line for the binary system acetone-butyl alcohol (Fig. 6) shows an initial rise from o to 10 percent butyl alcohol

from which point the curve follows a straight line. The surface tension curve for acetone and water lies between the pure components and shows a rapid rise as the percent water is increased. In the ternary system the binoidal curves pass through maxima, these being more pronounced as the percentage of butyl alcohol is decreased. The effect of the water on the system becomes more evident in the triangular diagram (Fig. 7) where the constant surface tension lines draw together as the percent water is increased.

Refractive Index. The refractive index curve (Fig. 8) for the acetone-butyl alcohol system is practically a straight line function of the composition. The refractive index line of the acetone-water system forms a smooth curve passing through a maximum at 70 percent acetone. As the butyl alcohol is increased, the intermediate curves all pass through maxima and are practically parallel to the acetone-water curve. These maxima are shown in the triangular diagram (Fig. 9) by the minimum at 70 percent acetone and 30 percent water.

Boiling Points. The boiling points (Fig. 10) of the system acetone-butyl alcohol lie on a smooth curve. The curve for the acetone-water mixtures are similar to the acetone-butyl alcohol curve but the slope of the former is not as great as the latter. The boiling points of the butyl alcohol-water mixtures pass through a minimum, this fact being shown on the binoidal curve when the acetone-butyl alcohol-water lines cross the acetone-water line. The acetone-butyl alcohol-water lines lie intermediate between the acetone-water and acetone-butyl alcohol lines. The triangular diagram (Fig. 11) shows that the boiling points are intermediate between those of the pure components.

A STUDY OF THE PARTICLE SIZE OF COLLOIDAL HYDROUS BERYLLIUM OXIDE SOLS*

BY WILLARD H. MADSON

Many of the properties of colloidal hydrous beryllium oxide sols are typical for metallic oxide sols. Continuing the study of the properties of these systems this investigation was undertaken to determine the size of colloidal oxide particles of these colloidal systems, and thus determine whether or not any of the properties are especially dependent upon the particle size.

Only a brief summary of the preparation of the sols used in this investigation need be given here. A detailed description of the preparation of the sols may be found in an earlier article on colloidal beryllium oxide sols by Madson and Krauskopf.[1] All the sols were dialyzed in the "Sorum" dialyzer[2] using collodion membranes and allowing about two liters of distilled water to flow through each battery each hour. The temperature of the bath, when heated, was about 80°C. (See Table I.)

TABLE I

Summary of the Purification of Hydrous Beryllium Oxide Sols

Sol. No.	Total no. hours dial.	Hours dial. hot	Mg. BeO per l
16d	168	162	51
17d(12)	12	12	86
17d(72)	72	68	65
18d	97	88	64

Determination of Particle Size

From among the dozen or more methods described in the literature,[3] the method of direct particle count was chosen as being the most convenient for this investigation. The visibility of the particles in the ultramicroscope depends chiefly upon two factors,[4] namely, "the strength of illumination, and on how greatly the refractive index of the particles differs from that of the dispersion medium. The difference between the two refractive indices must be adequate to allow a considerable diffraction of the light to take place at all. If dispersed phase and dispersion medium are only slightly different with respect to refractive power, one observes in the ultramicroscope only a uniform feeble brightening."

[1] Madson and Krauskopf: J. Phys. Chem., **35**, 3237 (1931).
[2] Sorum: J. Am. Chem. Soc., **50**, 1264 (1928).
[3] Kuhn: Kolloid-Z., **37**, 365 (1925).
[4] Freundlich: "Colloid and Capillary Chemistry," 387 (1926).

All sols studied by the author showed particles distinctly visible in the ultramicroscope. There was a slight scintillation which indicated that the particles were not spheres, but either disc or rod shaped.

The ultramicroscope used was of the slit type, the source of illumination being a 120-volt direct current arc drawing about six amperes. The liquid being examined was contained in a curvette fitted with quartz windows.

Since the particles of hydrous beryllium oxide exhibit Brownian movement, it is apparent that the number of particles in the field of view at any time will vary. It is also obvious that if there are too many particles in the field at once, the diffraction images will overlap to such an extent that the field will show simply a uniform brightening. The particle count must be made almost instantaneously. Therefore it is necessary to dilute the sol to such an extent as to make the individual particles easily distinguishable and also to such an extent that the number of particles present in the field of view at any time may be counted at a glance. The number present should range from two to five, although it is possible, with experience, to count as many as seven or eight at a glance, especially if the particles are grouped in certain arrangements. The dilution required is dependent upon the concentration of the original sol.

This dilution was accomplished by pipetting 100 m.l. of the original sol into a one-liter volumetric flask and diluting to the mark with distilled water; after thorough mixing, 50 m.l. of this liquid were pipetted into another volumetric flask and water added to make 250 m.l. This dilution of 1–50 was found to be suitable for the particle count of all the hydrous beryllium oxide sols studied in this investigation.

A disc of copper foil which had been pierced in the center by a needle was interposed in the eye-piece of the microscope, thus limiting the field of view. The volume of the field was then determined in the manner described by Ayres and Sorum.[5]

In order to get a statistical average of the particles in the field at one time, the counts must be made at regular intervals. This was accomplished by means of a motor driven disc. The annular opening near the outer edge of the disc was three-fourths covered with red celluloid; the other one-fourth was left open to allow the free passage of the beam of white light. This disc was placed between the slit and the condensing lens of the microscope. By means of this arrangement the position of the particles could be followed in the field of view. They appeared as red points of light for three-fourths of the time and white points one-fourth of the time. The count was made when the color changed to white. The disc was rotated at the rate of one revolution in four seconds; the counts were made at regular intervals of four seconds, one second being allowed for the actual count. Zsigmondy[6] indicates that one hundred to two hundred counts should be made on each sol. However, in this study, a larger number of counts was made—between three hundred fifty and four hundred counts. The counts were made on from three to five different samples

[5] Ayres and Sorum: J. Phys. Chem., **34**, 878 (1930).

[6] Zsigmondy: "Colloids and the Ultramicroscope," 120 (1909).

of the sol. The average number of particles in the field at any time was obtained by dividing the total number of particles counted—that is, the sum of the individual counts—by the number of counts made.

The number of particles present in one m.l. of the original sol was calculated from the average number of particles in the field at any time, the volume of the field, and from the amount the sol was diluted. The average volume of a hydrous beryllium oxide particle was calculated from the analysis of the sol for beryllium oxide content and on the assumption that the density of the colloidal hydrous beryllium oxide is the same as the density of beryllium oxide in the precipitated state. Assuming spherical or cubical particles, the length of the cube edge or diameter of the sphere is readily calculated. Assuming a cube, the cube edge may be calculated by the following simple formula:

$$\text{cube edge in cm.} = \sqrt[3]{\frac{\text{vol. field in c.c.} \times \text{g.BeO per c.c. orig. sol}}{\text{parts. per count} \times \text{dilution} \times \text{density BeO}}}$$

Assuming a sphere, the radius of the sphere may be calculated from the average volume of the particle, using the well known formula for the volume of a sphere $V = 4/3\pi r^3$, which gives $r = \sqrt[3]{\frac{3 V}{4 \pi}}$.

Following is a typical calculation based on the data from sol No. 17d(72):

Diameter of field	0.03 m.m.
Depth of field	0.03 m.m.
Volume of field	2.12×10^{-8} m.l.
Density of BeO	3.02
Particles counted	981
No. of counts	407
Average per count	2.42
Dilution of sol	1–50
g. BeO per m.l. of orig. sol	0.000065

In 2.12×10^{-8} m.l. there are 2.42 particles, therefore in one m.l. there are $2.42/(2.12 \times 10)^{-8} = 1.14 \times 10^8$ particles. The dilution was 1–50; in one m.l. of original sol there are $50 \times (1.14 \times 10^8) = 5.7 \times 10^9$ particles. The weight of each particle is $0.000065/(5.7 \times 10^9) = 1.14 \times 10^{-14}$ g. Assuming the density to be 3.02, the volume of each particle is $(1.14 \times 10^{-14})/3.02 = 3.78 \times 10^{-15}$ m.l.

If particle is a cube:

$$\text{edge} = \sqrt[3]{3.78 \times 10^{-15}} = 1.56 \times 10^{-5} \text{ cm.}$$
$$= 156 \ \mu\mu.$$

If particle is a sphere:

$$r^3 = \frac{3.78 \times 10^{-15}}{4.189} = 0.901 \times 10^{-15}$$
$$r = \sqrt[3]{0.901 \times 10^{-15}} = 0.97 \times 10^{-5} \text{ cm.}$$
$$r = 97 \ \mu\mu.$$

Table II gives a summary of the particle counts and particle sizes deter-
mined in this investigation.

<div align="center">TABLE II</div>

<div align="center">Summary of the Determination of the Particle Size of
Various Hydrated Beryllium Oxide Sols
(dilution 1–50)</div>

Sol No.	Hrs. dialyzed	No. Particles counted	No. of counts	Av. No. of particles per count	Edge if particle is a cube	Radius if particle is a sphere
17d(12)	12	1242	353	3.52	151 $\mu\mu$	94 $\mu\mu$
17d(72)	72	981	491	2.42	156	97
18d	97	927	419	2.21	160	99
16d	168	903	395	2.28	147	91
				Average size	153.5	95.3

<div align="center">Discussion</div>

Obviously this method of direct particle count gives only the upper limit
for the particle size, for any amicroscopic particles could not be seen in the
microscope and therefore were not counted. However, such particles were
included in the analysis of the sol for beryllium oxide content.

The calculations of the particle size are based on the assumption that the
density of beryllium oxide and the colloidal beryllium oxide particle are the
same, which is not very probable. Madson and Krauskopf[1] state that the
colloidal hydrous beryllium oxide coagulum contains less than one molecule of
water for every two molecules of beryllium oxide. The author has recently
repeated the determination and obtained the same results. Generally the
hydroxides are less dense than the corresponding oxides. With such a small
amount of hydration, the density of the colloidal particles would be expected
to be but slightly less than the oxide. A 25 percent decrease in density will
diminish the cube edge less than 10 percent. Therefore even if the density of
the particle is considerably less than that of the oxide, the size of the particle
as calculated would not be increased an appreciable amount.

The particle sizes of 151, 156, 160, and 147 $\mu\mu$ for sols dialyzed 12, 72, 97,
and 168 hours respectively, show that the particle size is not directly dependent
upon the length of time of dialysis for the particle size does not increase with
the length of time of dialysis (a sol dialyzed 12 hours has larger average particle
size than the sol dialyzed 168 hours). Thus it seems that most of the particles
in colloidal hydrous beryllium oxide sols are comparatively large.

All stable purified colloidal hydrous beryllium oxide sols that have been pre-
pared have been very dilute, less than one hundred milligrams of beryllium
oxide per liter of sol. Since some of the properties of beryllium chloride are

comparable to those of ferric chloride, it seems reasonable to expect that sols of molar concentrations comparable to those of hydrous ferric oxide sols could be prepared. However, both the slight hydration and the comparatively large size of the colloidal particles tend to make them difficult to prepare. Apparently conditions of preparation must be developed which will increase the hydration of the particles or decrease their average size, or both, if concentrated stable sols of colloidal hydrous beryllium oxide are to be prepared.

Summary

1. Particle size in four colloidal hydrous beryllium oxide sols has been determined by direct particle count and found to range from 147 $\mu\mu$ to 160 $\mu\mu$, the mean size being 153.5 $\mu\mu$ for the cube edge.

2. A discussion of the rather large particle size has been given.

"THEORY OF COPRECIPITATION." THE FORMATION AND PROPERTIES OF CRYSTALLINE PRECIPITATES

BY I. M. KOLTHOFF

1. Introduction

It has been known for a long time that crystalline precipitates separating from a solution are not, as a rule, quite pure but usually contain imperfections of mother liquor with foreign constituents. A vast number of empirical facts pertaining to the presence of various impurities in crystalline precipitates may be found in the analytical literature. Unfortunately, these data are of not much use in the interpretation of the so-called "coprecipitation" or "carrying down," mainly for the reason of poor description of experimental conditions. As will be shown later in this paper, the latter are of primary influence as regards the kind and amount of coprecipitation. Moreover, it has been a general custom in analytical chemistry to use the words, coprecipitation, carrying down, occlusion, inclusion and adsorption as collective names, meaning nothing else but the establishment of the fact that impurities are carried down with or in a precipitate. In a systematic treatment of the problem, it should be emphasized, however, that *three different phenomena mainly* account for the *presence of impurities in the precipitate* and in a study of the problem, it is necessary first to find out what kind of coprecipitation we are dealing with. In this paper, three cases are distinguished:

a. *The formation of mixed crystals.* In this case the impurities are *incorporated* in the *crystal lattice* and they do not change the regular structure of the latter. The amount of mixed crystal formation depends as in case C upon adsorption phenomena during the growth of the precipitate.

b. *Occlusion.* In this case the impurities are not incorporated in the crystal lattice, but *they are adsorbed during the growth of the crystals* and give rise to the formation of *imperfections* in the crystal. ("Hohlräume or Locker-stellen" (Smekal); or centra of activity—(H. S. Taylor).) Here adsorption phenomena during the growth of the crystals are mainly responsible for the amount of occlusion. It is especially with this kind of coprecipitation that we are concerned in this paper.

c. *Surface adsorption by the precipitate after it has been formed or separated.* This kind of coprecipitation is only of practical importance when the precipitate has a large surface, i.e. when it behaves like a flocculated colloid. If the precipitate has a definitely micro-crystalline character (as observed under the microscope) the amount of coprecipitation caused by surface adsorption is, as a rule, of no practical significance. Confusion is caused in the analytical literature by the fact that certain phenomena have been attributed to coprecipitation (an expression often used to indicate that a precipitate is not quite pure), but which have nothing to do with it. This may be illustrated by two examples.

In most text books of analytical chemistry, it is mentioned that magnesium is coprecipitated with calcium oxalate. Although there is actually a slight coprecipitation of this element, the presence of magnesium in calcium oxalate, if the latter is precipitated from solutions containing much magnesium salt, is mainly due to the slight solubility of magnesium oxalate. If relatively much magnesium is present and an excess of oxalate is added, the solution becomes supersaturated with respect to magnesium oxalate. First of all, calcium oxalate precipitates and then on standing magnesium oxalate crystallizes out slowly. Therefore, we are not dealing here with a case of coprecipitation, but of *post-precipitation*, the crystals of calcium oxalate being not at all or only slightly contaminated by magnesium. The magnesium oxalate crystallizes out as a separate phase. A detailed investigation of coprecipitation with calcium oxalate is being made in this laboratory by E. B. Sandell; the results will be described in his doctor's thesis and communicated later. Another example of post-precipitation is the so-called "coprecipitation of zinc with copper sulfide." In an extensive investigation[1] it has been shown that here again we are dealing with a case of post-precipitation. In relatively weakly acid medium a solution saturated with hydrogen sulfide is supersaturated with respect to zinc sulfide. First of all, the copper sulfide precipitates according to the laws of fractional precipitation; on standing zinc sulfide separates out slowly. Even in the more recent literature, this "post-precipitation" of zinc sulfide is described as a coprecipitation although it has nothing in common with it. Of course, it is quite possible that the primary precipitate has a promoting effect upon the separation of the secondary precipitate as in the copper sulfide-zinc sulfide case, the precipitation of zinc sulfide is enhanced at the surface of copper sulfide. It should be clearly understood however, that the secondary precipitate is not carried down by the primary precipitate and that we are not dealing here with a real case of coprecipitation.

d. A case which rarely occurs is that coprecipitation actually has to be attributed to the formation of a definite chemical compound. The so-called coprecipitation of alkali oxalate with lanthanum oxalate is caused by the formation of a double oxalate as has been shown by I. M. Kolthoff and R. Elmquist.[2] From experiments of Z. Karaoglanov and B. Sargotschev,[3] it appears that coprecipitation of lead bromide and lead chloride with lead oxalate is due to the formation of a double salt $(PbX)_2Ox$. However, the formation of such definite chemical compounds is very seldom encountered in analytical work, although it should not be overlooked as a possible interpretation of the presence of much "impurity" in the precipitate.

In this paper an attempt is made to formulate a general theory of coprecipitation, especially of the kind specified in Sub. b. The hope is expressed that such a theory will not only contribute to the understanding of the formation of impurities in precipitates formed under analytical conditions and

[1] I. M. Kolthoff and E. Pearson: J. Phys. Chem., **36**, 549 (1932).

[2] Kolthoff and Elmquist: J. Chem. Soc., **53**, 1232 (1931).

[3] Karaoglanov and Sargotschev: Z. anorg. allgem. Chem., **199**, 7 (1931).

thereby the improvement of the exact precipitation procedures, but will also have a wider bearing on the problems of mineralogical formations and the properties of slightly soluble micro-crystalline precipitates.

It should already be mentioned here that in recent years various authors have tried to treat the problem of coprecipitation from a more general view point. However, no sharp distinction has been made between the various kinds of coprecipitation as is done in this paper.

In the following a short discussion will be given of the formation and properties of precipitates which is of importance with regard to the general problem. More detailed information will be given in consecutive papers which will contain the results of experimental studies being made at the present time in our laboratory.

2. The Thermodynamic Potential of Crystals

An ionic lattice, according to the precipitation rule of Paneth-Fajans[4] has a strong adsorbing action for ions which form a slightly soluble or slightly dissociated compound with ions of the lattice of opposite charge.

It seems advisable to distinguish between primary and secondary adsorption of ions by an ionic lattice. If silver chloride, for example, is shaken with an alkali chloride solution, there is a primary adsorption of chloride ions. Owing to the fact that the system must be electrically neutral an equivalent amount of any kind of foreign cations has to be adsorbed as well (secondary adsorption). A preferential adsorption of those cations will take place, whose compounds with the primary adsorbed ions are slightly soluble or slightly dissociated. This rule should be correlated with the following: The higher the valence of the ions with a charge opposite to that of the primary adsorbed ions, the stronger they will be adsorbed. This may be inferred from measurements made by L. Imre[4a] on the adsorption of actinium, thorium B and radium by negatively charged silver iodide and could be expected already from the similarity between flocculation of colloids and adsorption of ions by a particle. If the lattice surface does not contain an excess of its own ions there may be a primary adsorption of foreign ions. These will be held by much less stronger forces than the lattice ions and as a rule will easily be replaced by the latter.

K. Fajans and W. Frankenburger[5] give a very clear picture of what occurs when a crystal lattice is in contact with a solution containing an excess of one of its own ions.[6] "The crystal lattice adsorbs one of the kind of ions constituting it. The adsorption forces are here identical in nature with those holding the adsorbent together . . ." "If we assume, for simplicity, a difficultly soluble salt, both of whose ions are equally strongly adsorbed on the

[4] F. Paneth: Physik. Z., 15, 924 (1914); K. Horovitz and F. Paneth: Z. physik. Chem., 89, 513 (1915); Wien. Ber., 123, II^a, 1819 (1914); K. Fajans and P. Beer: Ber., 46, 3486 (1913); Fajans and K. Richter: 48, 700 (1915); O. Hahn, O. Erzbacher and N. Feichtinger: Ber., 59, 2014 (1926); O. Hahn: Naturwissenschaften, 14, 1196 (1926).)

[4a] L. Imre: Z. physik. Chem., 153 A, 127 (1931).)

[5] K. Fajans and W. Frankenburger: Z. physik. Chem., 105, 255 (1923).

[6] Ref. 5, page 270.

same crystal lattice, i.e. in contact with the saturated solution containing both ions in equal concentration, there arises no potential difference between salt and solution. If we add an excess of one of the ions, say the cations, the adsorption equilibrium of this ion on the anions of the lattice will be disturbed and consequently the cations will be deposited on the anions of the lattice covering them in part and giving the lattice a positive charge. The equilibrium with the anions in the solution is thereby also disturbed as can easily be seen from the fact that the anions of the lattice which are covered by positive ions are removed from kinetic contact with the solution and that the surface now carrying an excess of positive charge exerts an increased attraction on anions of the solution. Fresh anions must, therefore, be deposited on the crystal lattice from the solution until a new state of equilibrium is set up with a smaller concentration of anions. This means that the solubility of the salt is lowered by an excess of cations. It is clear that a closer investigation of the whole adsorption isotherm of both ions must give a quantitative connection with the law of solubility product. Two points can clearly be seen: Since the adsorption of cations in the case considered is greater, the greater the excess added to the solution so must the amount of anion precipitated increase likewise and the solubility decrease corresponding entirely quantitatively with the law of mass action." In excellent papers J. A. V. Butler[7] has already shown that there is no reason to expect that a crystal lattice will adsorb cations and anions equally well. "It may obviously happen that the tendency of one of the ions to go in solution may be greater than that of the other ion owing either to a smaller attraction by the lattice or a greater attraction of the solvent for this ion." To this statement may be added the fact that the conditions under which the thermodynamic potential will be equal to zero will be different in different solvents, since the activities of various ions change in a different way in going from one solvent to another.

H. R. Kruyt and P. C. van der Willigen[8] in harmony with Butler's statement found that crystals of silver iodide in contact with the saturated solution in water assume a negative charge, thus showing a preferential adsorption of the iodide ions. Butler succeeded in showing that the expression for the solubility product holds only by considering the kinetic equilibrium between solution and solid.

From the above it is evident that any crystal in equilibrium with its solution always will adsorb ions of its own kind, if they are present in excess in the solution; only under one condition, either in a saturated solution in water (if the adsorption potential of the anions equals that of the cations) or in presence of a slight excess of anions (adsorption potential of anions smaller than that of cations) or in presence of a slight excess of cations (adsorption potential of anions larger than that of cations) will the thermodynamic potential be equal to zero.

[7] J. A. V. Butler: J. Phys. Chem., **28**, 438 (1924); Trans. Faraday Soc., **19**, 659, 729, 734 (1924).

[8] H. R. Kruyt and P. C. van der Willigen: Z. physik. Chem., **139**, 53 (1928).

In considering the adsorption by a crystalline precipitate during its growth it will be seen that this thermodynamic potential primarily determines the amount of coprecipitation. Quantitatively there is a simple relation between the thermodynamic potential and the corresponding ion concentration in the solution as has been shown by F. Haber.[9] The same expression is found as the one that holds for the potential difference between an electrode and a solution containing ions which the electrode can send into solution (Nernst's equation);

$$E = -\frac{RT}{nF} \ln a_{ion} + Const.$$

a_{ion} is the activity of the ion.

It is singular that no analytical application has been made of this relation between thermodynamic potential of a crystal lattice and a solution containing ions which are the building stones of the lattice. It may be expected, for example, that a barium sulfate electrode will behave as a specific electrode for barium—and sulfate ions. With the present development of the technique of measuring the electromotive force of cells with extremely high resistances, a wide field of potentiometric measurements may be anticipated.

The relation between thermodynamic potential and the amount of ions adsorbed has been determined in the case of silver iodide by E. Lange and R. Berger[10] who found that the change of the thermodynamic potential is proportional to $\ln C_{ion}$ in the solution and up to a certain limit to the concentration of adsorbed ions on the surface.

3. Solubility and Particle Size

For many years it has been known that the solubility of crystals of very small size is larger than that of crystals of large dimensions[11] owing to the greater surface energy of the former. If the crystal size becomes smaller than 1 to 2μ the solubility quite generally increases with increasing surface development. The most extensive and interesting experiments in this field have been carried out by M. L. Dundon and E. Mack,[12] who also have given corrected values for the classical data of G. A. Hulett[13] on the solubility and crystal size of gypsum. Although the order of magnitude of the surface tension of various crystals as calculated by Dundon is probably correct no claim is made for great exactness of the figures. The particle size was approximated by microscopic measurements, involving a relatively large uncertainty at small dimensions, and it was assumed that the crystals were quite compact, i.e. the presence of capillaries (inner surface) was not considered. More-

[9] F. Haber: Ann. Physik, **47**, 26, 947 (1908); F. Haber and Z. Klemensiewicz: Z. physik. Chem., **67**, 385 (1909).

[10] E. Lange and R. Berger: Z. Elektrochemie, **36**, 171 (1930).

[11] For literature review compare H. Freundlich: "Kapillarchemie," 2nd Ed., 207-211 (1922); R. A. Gortner: "Outlines of Biochemistry," 150 (1929); T. B. Smith: "Analytical Processes," 239-278 (1929).

[12] M. L. Dundon and E. Mack: J. Am. Chem. Soc., **45**, 2479 (1923); M. L. Dundon: **45**, 2658 (1923).

[13] G. A. Hulett: Z. physik. Chem., **37**, 385 (1901); **47**, 357 (1909).

over the following paradoxical phenomenon has not been adequately explained: If coarse crystals of barium sulfate were added to a saturated solution in equilibrium with crystals of very small size the solubility decreased gradually and finally became equal to the "macroscopic solubility" (normal solubility), although by microscopic examination a great number of particles of original small size appeared to be present. In order to explain this peculiar fact Dundon considers one of the two alternatives; either that originally many particles had been present which were too small for microscopic measurement (which would mean that none of the data in the following table are correct) or that soon after a saturated solution in equilibrium with the small particles has been formed the solubility of the smaller particles is decreased by some adsorption effect such as the acquisition of a charge. According to Dundon, the latter assumption seems to be in harmony with the facts. However it cannot be denied that this explanation is far from being satisfactory. The adsorption process takes place rather quickly and it is hard to accept the view that the particles do not acquire a charge until a saturated solution has been formed. Moreover experimentally the influence of the charge of a particle on its solubility has never been shown although W. C. McC. Lewis[14] and L. F. Knapp[15] in more or less mathematical papers show that the charge opposes the surface tension and hence tends to decrease the solubility. The charge increases with decreasing size and the solubility reaches a maximum at certain dimensions, and decreases with increasing surface development. Without entering into a detailed discussion it should be realized that the solubility decreases with increasing thermodynamic potential of the particles, as has been mentioned in the preceding paragraph; experimentally however it has never been shown that the electrokinetic potential exerts a similar influence; and on thermodynamic grounds this is not to be expected.

There is much more reason to assume that on account of the charge or the presence of an ion atmosphere around the particle the speed of exchange of ions between surface and solution (the kinetic equilibrium between solution and deposition velocity) is materially inhibited. This may give an explanation of the peculiar fact that the crystals of small dimensions disappear so slowly if macroscopic crystals are added to their saturated solution. At the surface of the large crystals, the solution and deposition equilibrium is established much more quickly than at the surface of the charged particles of small size. If the large and small crystals are both present as solid bodies the state of equilibrium between the former and the solution is readily established; the small crystals very slowly send more ions into the solution, which then are deposited on the surface of the large crystals; in other words the latter grow *very slowly* at the cost of the small sized particles. Since the solution rate of the latter is so small it will require a long time before all small particles have disappeared. This explanation based on the difference between solution and deposition rate at the surface of small and large crystals readily accounts

[14] W. C. McC. Lewis: Kolloid-Z., 25, 91 (1909).
[15] L. F. Knapp: Trans. Faraday Soc., 14, 457 (1921/22).

for the fact that a normal solubility is found if the small particles are present with the larger size crystals.

This interpretation is in harmony with recent experiments of P. S. Roller[16] on the relative rate of solution of gypsum. Down to a diameter of 25μ he found the rate of solution to be proportional to the specific surface, and the dissolution factor was a constant. Below 25μ the rate of solution increased more rapidly than the surface exposed until at a size of 2.8μ the dissolution factor reached a maximum. At smaller dimensions it decreased again, probably on account of acquisition of a charge.

Assuming, then, that Dundon's data at least give the order of surface tension of various crystals it is possible to explain with their aid some facts which so far have been more or less obscure in analytical chemistry. In the following table a summary of Dundon's results is given.

TABLE I

Surface Tension of Some Substances according to M. L. Dundon

Substance	M	ξ	Mol. Vol.	r (μ)	% Increase Solubility	Temp. °C	σ	Hardness
PbI_2	461	6.16	74.8	0.4	2	30	130	Very Soft
$CaSO_4.2H_2O$	172	2.32	74.2	0.2–0.5	4.4–12	30	370	1.6–2
Ag_2CrO_4	332	5.52	60.1	0.3	10	26	575	Appr. 2
PbF_2	245	8.24	29.7	0.3	9	25	900	” 2
$SrSO_4$	184	3.96	46.4	0.25	26	30	1400	3.0–3.5
$BaSO_4$ (Hulett)	233	4.5	52	0.1	80	25	1250	2.5–3.5
(Dundon)				0.2	90	30	3000	
CaF_2	78	3.18	24.6	0.3	18	30	2500	4

M denotes molecular, weight, ξ density of crystal; Mol. Vol. molecular volume: r is radius of particle expressed in microns (microscopically measured), σ is surface tension of particle, % Increase Sol. is per centum increase of solubility with regard to massive crystals.

If we consider slightly soluble salts the saturated solutions of which are completely dissociated into the ions and whose activity coefficients can be put equal to 1 the relation between increase of solubility on the one hand and the size of crystals and their surface tension on the other, can be represented by the equation

$$\frac{R\,T}{M}\ln\frac{Sr}{S} = \frac{2\,\sigma}{\xi\,r}$$

R is the gas constant, T the absolute temperature, M the molecular weight, Sr the solubility of particles with a radius r, S the same of normal crystals, σ the surface tension and ξ the density.

By means of this equation and Dundon's data the ratio Sr/S for barium-sulfate, silver chromate and lead iodide at a size of 0.04μ (r= 0.02μ) was calculated.

[16] P. S. Roller: J. Phys. Chem., **35**, 1133 (1931).

$$BaSO_4 \frac{S_{0.02}}{S} = 930$$

$$Ag_2CrO_4 = 4.0$$

$$PbI_2 = 1.38$$

Whereas at this small size the solubility of barium sulfate is about 1000 times larger than that of the large crystals, the solubility of silver chromate under the same condition has increased only 4 times and that of lead iodide only 1.4 times.

These differences explain the fact that substances of about the same solubility and precipitated under analogous conditions behave in an entirely different way. Silver chloride and barium sulfate have a solubility product of the same order of magnitude; in spite of this, silver chloride is always precipitated as a flocculated colloid, barium sulfate as microcrystals under analytical conditions. It is easy now to account for this difference. Suppose a barium solution is added to a sulfate solution and silver ions are added to a chloride solution under such conditions that the *"macroscopic supersaturation"* of barium sulfate and silver chloride are the same. The silver halides form soft crystals[17] and their solubility is more or less independent of the crystal size: in other words, the solubility of the particles first formed in the solution (nuclei) is about the same as that of large size crystals. For barium sulfate (strontium sulfate, lead sulfate, etc.) the case is quite different. The solubility of the primary particles is much larger than that of the large crystals: therefore the solution is much less supersaturated with respect to the small particles of barium sulfate than of silver chloride. The velocity of formations of nuclei and growth of the latter to large crystals increases with increasing supersaturation. Therefore the formation of nuclei is much more spontaneous in the case of silver chloride than of barium sulfate; by the rapid formation of so many nuclei the solution is soon exhausted and no ions are left in solution to contribute to a growth of the small particles; the silver chloride precipitates as a flocculated colloid. In the case of barium sulfate much less nuclei are formed, which grow at the cost of the ions left in the solution; the slightly soluble substance finally settles as a microcrystalline precipitate. From the above it is evident that Böttger's[18] relation between sensitivity of a precipitation reaction and solubility:

$$E = L + S$$

in which E represents the sensitivity, L, the solubility and S the visibility of the particles has no general validity. It will only hold[19] if the "micro" and "macro" solubilities of the substance are approximately the same as in the case of silver halides. But if this condition is not fulfilled, which is very often the case (barium sulfate, strontium sulfate, calcium oxalate) there is no simple relation between solubility and sensitivity of the reaction.

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[17] Comp. A. Reis and L. Zimmermann: Z. physik. Chem., **102**, 299 (1902).

[18] Comp. W. Böttger: Chem. Ztg., **33**, 1003 (1909); M. Gorski: Z. anorg. allgem. Chem., **81**, 315 (1913); W. Böttger: Chem. Ztg., **36**, 1097 (1912); Z. angew. Chem., **25**, 1992 (1912).

[19] I. M. Kolthoff: Böttger Festschrift, Z. anal. Chem., **86**, 34 (1931).

The velocity of recrystallization of finely divided precipitates is also determined by the relation between solubility and surface tension. It is well known that finely divided precipitates of barium sulfate, calcium oxalate, etc., which are formed in not too dilute solution on standing crystallize to large crystals; with silver chloride, such a recrystallization does not take place, because the difference in solubility between the small and large size crystal is too small. Only if the supersaturation is made very slight is it possible to obtain large crystals of silver chloride (recrystallization from ammonia).

It is not very easy to find suitable examples for the demonstration of validity of the mass law expression. A "saturated solution" of silver chloride or lead iodide gives almost instantaneously a precipitate with excess of one of the two ions; the experiment does not succeed with lead sulfate, strontium sulfate, calcium oxalate, etc. V. Chlopin[20] reports that he was able to prepare stable lead sulfate solutions which were more than 1000 times supersaturated. The explanation is simple again, the solution is supersaturated only if inoculated with large crystals, but it is not necessarily supersaturated with respect to the primary particles formed at the beginning of crystallization.

Considering then crystallization from a solution it may quite generally be said that *supersaturation is a relative conception:* the supersaturation cannot be expressed in an absolute figure unless crystals of the normal solubility are present as solid body.

4.   Filterability of Precipitates

It is the usual practice in analytical chemistry to heat precipitates and mother liquor after precipitation for some time in order to obtain a more readily filterable precipitate by recrystallization.[21]

In the preceding chapter however we have seen that the process of recrystallization of very small particles is extremely slow. Dundon[12] for example boiled a suspension of barium sulfate (size 0.2 to 0.3μ) under a reflux condensor for a week with no visible change of particle size even when seeded with large crystals. From experiments made by Professor Bigelow, H. M. Trimble[22] expected that the rate at which larger crystals of a nearly insoluble substance grow at the expense of smaller ones in contact with the saturated solution must be very low, probably too low to account for coalescence of the precipitate as it occurs in analytical chemistry. Experimentally this was shown to be true. Finely divided barium sulfate digested for a few hours in the presence of some hydrochloric acid at 100° was readily filterable if not stirred during digestion. Microscopic examination showed that the average size of the small particles (between 1 and 4μ) remained unchanged during digestion. If the mixture was stirred during the digestion, no clear filtrate was obtained even after three to four days.

[20] V. Chlopin: Naturwissenschaften, **17**, 959 (1929).

[21] Comp. Wi. Ostwald: "Grundlagen der analytischen Chemie," **14**, 22 (1894).

[22] H. M. Trimble: J. Phys. Chem., **31**, 601 (1927).

From these and analogous experiments Trimble inferred that the "co-alescence" of an unfilterable precipitate to give a filterable one, cannot be explained in terms of growth of the larger particles at the expense of the smaller ones. During the digestion without stirring the particles come into close contact with one another and form aggregates which adhere firmly. As digestion proceeds, barium sulfate either from supersaturated solutions or from dissolution of very small particles, deposits upon these aggregates and cements them together. This effect is enhanced when the solution is allowed to cool. On the other hand, when digestion is accompanied by stirring, all crystals grow alike at the expense of any material which may be separating from solution; there is no opportunity for cemented aggregates to form. With E. B. Sandell, the writer has made various experiments with

A.
Movable Double Layer
(colloid)

B.
Flocculated
(X in lattice)

C.
Flocculated
(Probable case)
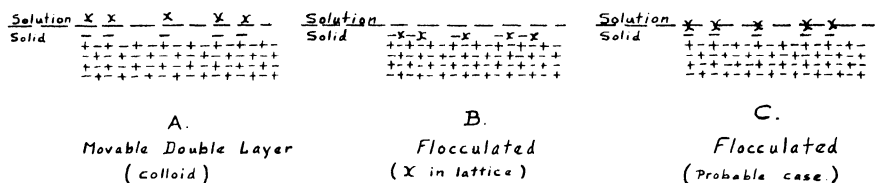
Fig. 1

suspensions of barium sulfate, calcium oxalate monohydrate, silver chloride, etc. It was observed that after digestion with or without stirring for one to two days, a distinct growth of crystals took place. Even in a silver-chloride suspension it was possible to observe small crystals under the microscope after heating for a day. Still it is true that in any case, after prolonged heating, a vast amount of the small particles is present with the original size. In the preceding chapter it has been shown that recrystallization of charged particles is a slow process.[23] On the other hand it is also true that suspensions which originally did not yield filterable precipitates gave clear filtrates after digestion. Under the microscope one gets the impression that the small particles of the precipitate are held together in a film after digestion. The problem of filterability then is reduced to the question, why the particles of a flocculated sol glue together. In textbooks on colloid chemistry this problem is not discussed. A priori it is not to be expected that small particles will grow together. If a flocculated particle possessed a pure crystal surface one could accept the view of K. Fajans and von Beckerath[24] that the small particles will grow together with loss of energy, the negative ions in the surface of one lattice being attracted by those of opposite sign of the other lattice. However, it is hard to assume that the picture is as simple as this. Suppose in Fig. 1 "A" represents a particle of silver chloride, which is kept in colloidal solution by an excess of chloride ions. After destruction of the diffuse electrical double layer the picture is that represented by B or C. It is

[23] Many examples may be found in P. P. von Weimarn's monograph: "Die Allgemeinheit des Kolloidzustandes. Kolloides und kristalloides Lösen von Niederschlägen" (1925).

[24] K. Fajans and von Beckerath: Z. physik. Chem., 97, 478 (1921).

not to be expected that every kind of flocculating ion (X) can be incorporated in the crystal lattice (C), in other words forms mixed crystals and therefore C represents the most usual case after the flocculation. The surface of the other flocculated particles will have a similar appearance and there is no direct reason why the flocculated particles will lay their surfaces together (cement together). It is much more reasonable to assume that at the moment of flocculation the particles will repel each other; an impression which is actually obtained in observations under the ultramicroscope. This problem will be studied more extensively in Professor Gortner's laboratory. The flocculating ions X (Fig. 1) which are adsorbed at the surface of the floccu-lated particle are still able to exert a polarizing effect upon the solvent, in this case water, which means that they are more or less hydrated. It is a well known fact that a flocculated colloid contains large amounts of water. If the hydration is great enough a water layer will be formed around the particle, which, on account of its high curvature will have a tendency to decrease its surface. This may be accomplished by aggregation of various particles which in this way share their water jacket, thus giving the impres-sion of a film formation. In this manner it is also possible to explain why the rate of solution and of deposition of ions from the solution on the surface is so strongly inhibited, for the surface of the flocculated particles is more or less isolated.

Before drawing further conclusions, an experimental study is necessary to show whether the view offered here gives a true account of the facts. In a quantitative treatment, the orientation (polarization) of the water molecules around the particles should be considered.

5. The Formation of Precipitates. Amorphous and Crystalline Precipitates

An exhaustive treatment at this place of the speed of formation of nuclei and of growth of small crystals would require more space than is allowable. There is a special lack of exact data in the literature on the speed of formation of nuclei from supersaturated solutions; it may be expected that this speed will be proportional to the degree of supersaturation if the latter is expressed with regard to the solubility of the nuclei (v. i.). More is known of the speed of growth of crystals, especially from studies made by physicists.[25]

The speed of growth of crystals decreases on going from the corners to the edges and from thence to the planes. The speed of growth is not deter-mined by the rate of diffusion but by the speed with which the ions are adsorbed at the crystal surface. Constituents which change the adsorption equilibrium may have a tremendous influence on the speed of growth of various planes and the crystal habit finally obtained. Special reference is

[25] Comp. M. Volmer and I. Estermann: Z. Physik, 7, 13 (1921); 9, 193 (1922); Volmer and A. Weber: Z. physik. Chem., 119, 277 (1925); Volmer: Z. Elektrochemie, 35, 555 (1929); Volmer and M. Marder: Z. physik. Chem., 154 A, 97 (1931); K. Spangenberg: Z. Krist., 59, 403 (1924); H. Brandes: Z. physik. Chem., 126, 196 (1926); W. Kossel: Natur-wissenschaften, 18, 901 (1930); I. Stransky: Z. physik. Chem., 136, 259 (1928); 11B, 342 (1930); D. Balarew: Kolloidchem. Beihefte, 30, 249 (1930); 32, 205 (1931); for general dis-cussion comp. A. E. von Arkel and J. H. de Boer: "Chemische Binding als Elektrostatisch Verschijnsel," 248-286 (1930).

made to the work of R. Marc and collaborators[26] and more particularly to that of W. G. France and his students[27] on the influence of dyestuffs on the habit of various growing crystals. The problem of crystal growth is of extreme importance for that of coprecipitation because the amount of coprecipitated substance is greatly dependent upon the speed of formation of the crystals. This will be shortly discussed in the following chapter.

The form, shape, and size of a precipitate depends upon the experimental conditions. From all that has been said above, it is evident that a simple relation between supersaturation on the one hand, and the speed of growth and form of crystals on the other, as has been advocated by P. P. von Weimarn[28] cannot exist.

Although it cannot be denied that interesting statements and experiments of qualitative nature may be found in von Weimarn's numerous publications, his general equations are too simple and cannot be accepted. The velocity of formation of nuclei (condensation) during the first stage of the precipitation is formulated thus:

$$W = K\frac{Q - S}{S} = K\frac{P}{S} = K U$$

in which W is the initial rate of precipitation; Q the total concentration of the substance that is to precipitate, S the solubility of *coarse* crystals of the substance; $Q - S = P$ the amount of supersaturation and U the percentage supersaturation at the moment precipitation begins. Von Weimarn recognized that the velocity W of the first stage of precipitation could not be measured in actual practice and therefore, he introduced a specific coefficient called the "precipitate form coefficient" or "dispersity coefficient N," which is given by the expression:

$$N = P/S \; K_{ab} \; K_{ad} \; K_{bd} \; K_{ac} \; Z$$

in which Z is the viscosity, and K_{ab}, K_{cd} etc. represent the "physical and chemical association" of the substances AB, CD etc., which enter into the reaction AB (in solution) + CD (in solution) = AC (precipitate + BD (in solution). H. B. Weiser[29] remarks: "The significance of 'physical association' is known, but it is not clear what von Weimarn means by 'chemical association.'"

The growth of the nuclei depends not only on the degree of supersaturation, at a given moment, but also according to von Weimarn upon the diffusion coefficient:

$$V = D/d \; O \; (C-S)$$

[26] R. Marc and Wenk: Z. physik. Chem., **61**, 385 (1908); **68**, 104 (1910); **73**, 685 (1910); **75**, 710 (1911); **79**, 71 (1912).

[27] T. S. Eckert and W. G. France: J. Phys. Chem., **34**, 724 (1930); F. G. Foote, F. C. Blake and W. G. France: **34**, 2236 (1930); W. G. France: Colloid Symp. Ann., **59** (1930); especially C. H. Saylor: J. Phys. Chem., **32**, 1441 (1928).

[28] P. P. von Weimarn: "Zur Lehre von den Zuständen der Materie" Bd I Text, Bd II (1913); "Die Allgemeinheit des kolloiden Zustandes" (1925).

[29] H. B. Weiser: "The Colloidal Salts" (1928); for a discussion of von Weimarn's theory see also T. B. Smith: "Analytical Processes," 263 (1930).

in which D is the diffusion coefficient, d the thickness of the adherent film, O the surface, C the concentration of the solution and S the solubility of the disperse phase.

Without entering too much into details, it is evident that von Weimarn's equations have no general quantitative bearing:

(a). In the equations of the speed of formation of the nuclei S represents the solubility of coarse crystals. In a preceding chapter we have seen that S is a function of the size of the crystals, and even the order of its magnitude may be quite different for nuclei and for larger crystals; the percentage supersaturation has no definite value.

(b). The equation for the speed of growth of the crystals cannot be accepted, since this rate does not depend upon the speed of diffusion but upon the speed of adsorption. All factors which influence the speed of adsorption of the ions during the growth may materially change the speed of growth and the habit of the crystals obtained.

(c). It is to be expected that the speed of formation of nuclei will be dependent not only upon the relative supersaturation but also upon the actual concentration of the reacting ions. The formation of nuclei in a solution ten times supersaturated with regard to calcium sulfate is much more rapid than in that of barium sulfate of the same supersaturation. That the actual concentration of the reacting ions is of primary significance may also be inferred from the studies of Sven Odén[29a] on the formation of precipitates. It should be mentioned that in most studies on the speed of precipitation the supersaturation was calculated on the basis of the solubility of the substance in pure water. Even if the difference between "micro" and "macro solubility" could be neglected the repression of the solubility by the common ion effect should be considered. On account of this omission most of these studies have no quantitative significance.

Of much more importance are the views of F. Haber[30] on the formation of precipitates. He considers primarily the following two factors: *aggregation velocity*, (called by Haber Häufungsgeschwindigkeit) and *orientation velocity*, (Ordnungsgeschwindigkeit). If the solubility limit is exceeded, the molecules or aggregates of molecules, will have a tendency to lay themselves together and to accumulate to give larger aggregates. This aggregation velocity is a function of the supersaturation; the larger the latter, the less regular the separated aggregates will be. Besides the supersaturation the absolute concentration of the reacting ions will also be of significance. The aggregates formed, in which the molecules are mixed in a more or less arbitrary manner, are not stable. By loss of energy they tend to reach a state of equilibrium, in which the mass is ordered in a regular way in a crystal lattice. The speed with which this process takes place is called the orientation velocity. It is evident that the form in which a precipitate separates depends upon the competition between the aggregation and orientation velocity.

[29a] Sven Odén: Ark. Kemi Mineral. Geol., 7, No. 26 (1920); 9, No. 23 (1925); No. 32 (1926).

[30] F. Haber: Ber., 55, 1717 (1922).

If the supersaturation is extremely large the aggregation velocity will dominate and the separated particles do not show an X-ray spectrum, in other words they are *amorphous*. On standing, (aging) the amorphous precipitate will slowly transform into a crystalline modification. The phenomena described can be observed in the precipitation of various extremely slightly soluble hydrous metal oxides and metal sulfides.[31]

The orientation velocity will vary for various substances. Strongly polar substances, such as silver chloride, for example, will have a high orientation velocity, comparable with the crystallization velocity of this kind of molecule from the vapor state. The more completely the central ion of a molecule is surrounded by the ions of opposite charge the weaker the electric field outside the molecule will be, because its electric effect is mostly compensated by the surrounding ions. Such molecules will show a small orientation velocity. From this point of view it is clear why precipitated cadmium hydroxide, for example, is never obtained in an amorphous form; hydrous ferric oxide, on the other hand, if precipitated from cold solutions is amorphous, but is transformed on aging, especially on heating into a crystalline product. Hydrous oxides of the quadrivalent cations, like those of thorium, cerium, zirconium, in which the central ion is more or less completely surrounded by the anions, always precipitate in an amorphous form and show on aging very little or no tendency toward crystallization.

In the slow preparation of colloidal suspensions according to the condensation method, crystalline sols are obtained; if the precipitation takes place quickly as under analytical conditions, amorphous precipitates may be formed. In the older literature, a sol was usually considered as an intermediate state in the process of formation and growth of precipitates, this appears not to be true; the sols are crystalline whereas it is quite possible to obtain many slightly soluble substances in an amorphous form.

It is of practical importance to consider the solubility of amorphous precipitates somewhat more fully. It does not seem justifiable to speak of an "amorphous *modification*" if by some wild growth an amorphous precipitate is obtained; at least if a "modification" is considered as a chemically homogeneous individual. The amorphous form consists of aggregates which are grown together in a more or less arbitrary manner; it is not stable but is undergoing continuous transformation into a more stable crystalline state. The solubility of the amorphous form therefore, will not only be quite different from that of the crystalline phase, but what is more important, the solubility will no longer be constant but depend upon the state in which the amorphous form happens to be at a certain moment. This inference is quite important because in analytical problems, such as the precipitation of slightly soluble hydrous oxides and metal sulfides, the mass action law as a rule is applied. The latter, however, holds only for stable modifications when there is equilib-

[31] For examples comp. F. Haber: (ref. 27); J. Böhm and H. Niclassen: Z. anorg. allgem. Chem., **132**, 1 (1923); G. F. Hüttig and collaborators: **187**, 1; **190**, 353, 364; **191**, 161; **192**, 187, 225; **193**, 81, 93, 100 (1930). Kolloidchem. Beihefte, **31**, 347 (1930); and especially R. Fricke: Z. anorg. allgem. Chem., **166**, 244 (1927); Kolloid-Z. **49**, 229 (1929).

rium between solution and solid phase. The amorphous form is not in internal equilibrium and, therefore, neither with the solution. If an amorphous hydrous oxide is precipitated under various conditions, the same solubility product can hardly be expected. The water present in the amorphous precipitate will also have a great influence upon the solubility. Suppose for example, that a hydrous aluminum oxide is precipitated by mixing aquo aluminum ions $Al(H_2O_6)^{+++}$ with hydroxyl ions. With the large aggregation velocity, the aluminum ions will carry part of their water into the amorphous precipitate, and the hydroxyl ions probably will keep part of the water molecules oriented by polarization. The water is a powerful dielectric, and by its presence in the precipitate, will diminish the force by which the aluminum and hydroxyl ions attract each other in the solid. Therefore, owing to the presence of water between the ions, the solubility of the amorphous hydrous aluminum oxide must be much greater than that of the crystalline modification. It cannot be expected that the solubility will remain a constant during the transformation of the amorphous into the crystalline form; it will gradually decrease until the entire precipitate is present as the crystalline modification. Neglect of these considerations has caused some unfortunate confusion in the literature.

In the rapid formation of precipitates, another point must be considered. If various crystalline modifications of a substance exist, there is always a possibility that a metastable form will separate out first. On standing the labile form will be transformed more or less rapidly into the stable modification thus causing an entire change of the internal structure. Berthelot,[32] for example, claimed that freshly precipitated silver iodide undergoes a transformation on standing, a fact not confirmed by the experiments of J. W. A. van Hengel.[33] In agreement with Berthelot, the latter found however, that freshly precipitated barium carbonate undergoes a structural change on aging. E. B. Sandell, in experiments carried out in this laboratory found that calcium oxalate di or tri hydrate was separated under conditions under which only the monohydrate is stable. In the interpretation of the change of the amount of coprecipitated substance with the time of standing, such allotropic changes must be considered.

6.   The Theory of Coprecipitation

In the introduction it was emphasized that the expression "carrying down" used as a collective term to indicate that a precipitate contains foreign constituents is misleading, and that first of all it should be decided whether the impurities are incorporated in the crystal lattice or form imperfections in the interior of the crystals or finally are adsorbed at the surface of the precipitate. The second group in which the impurities are present as imperfections in the crystals is the most common one and will be defined as "real coprecipitation."

[32] Berthelot: Ann. Chim. Phys. [5] 4, 181 (1875); 29, 242 (1883).

[33] J. W. A. van Hengel: De metastabiliteit der stof. Praecipitatie-reacties, Thesis Utrecht (1931). On theory see especially C. H. Saylor (ref. 27).

Mixed crystal formation: Although the phenomena of isomorphism and mixed crystal formation have been known for almost a century, it is only of relatively recent date that more general relations have been discovered between size of ions and mixed crystal formation. H. G. Grimm and collaborators[34] formulated three conditions which must be fulfilled for the formation of mixed crystals of polar compounds:

(1). The chemical building type must be the same.

(2). The lattice types must be similar.

(3). The lattice constants must be of the same order of magnitude.

Grimm already showed that the following systems form mixed crystals: $SrSO_4 + KMnO_4$; $BaSeO_4 + KMnO_4$; $BaCrO_4 + KMnO_4$; $BaSO_4 + KBF_4$; $KBF_4 + KMnO_4$. Grimm's studies are supplemented by the beautiful investigations of V. M. Goldschmidt[35] on the relation between crystal structure and lattice properties on the one hand and chemical constitution on the other. The laws of isomorphism and mixed crystal formation are laid down, especially in his seventh study.[35] Isomorphism he defines as the phenomenon that substances of analogous chemical formula show analogous crystal structure. Analogy of chemical formula means analogous "brutto formula" in respect to total number of ions and to the number of positive and negative building stones (ions). Analogy of crystal structure means that both substances possess a geometrically symmetrical elementary parallelopiped, in which a same number of atoms is arranged in a geometrically similar fashion in such a manner, that the kind of charge (positive or negative) of the individual crystal building stones correspond with one another in both structures. Isomorphism occurs if the relative size of the crystal building stones and the relative strength of their polarizability within certain limits are identical, assuming of course that the brutto formulas of both substances are the same. If not only the relative size, but also the absolute size of the building stones are the same, the conditions of mixed crystal formation are created, other conditions being the same. There is a certain tolerance with regard to similar size; it seems that mixed crystal formation is still possible if the radii of the ions does not differ more than 15%. With these rules it is understandable why $BaSO_4 - KMnO_4$; $BaSO_4 - PbSO_4$; $CaCO_3 - NaNO_3$ can form mixed crystals. Relatively little is known of the properties of mixed crystals, which are formed in analytical processes; especially of their stability. From studies of O. Ruff and E. Ascher[36] one would infer that mixed crystals are very unstable if one of the constituents is slightly soluble and the other readily soluble. Thus in the case of $CaCO_3 - NaNO_3$ Ruff and Ascher found practically no sodium nitrate in the crystals,

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[34] H. G. Grimm and G. Wagner: Z. physik Chem., **132**, 131 (1928); H. G. Grimm: **98**, 353 (1921); Z. Elektrochemie, **28**, 75 (1922); **30**, 467 (1924); Z. Kristall., **57**, 574 (1922); Handb. Physik, **24**, 581 (1927).

[35] V. M. Goldschmidt: esp. Geometrische Verteilungsgesetze der Elemente VII Die Gesetze der Kristallochemie, Videnskapssel Skrifter 1 Mat. Naturw. Klasse Det Norske Videnskaps Akad. i Oslo I 1926; No. 2; Utgitt for Fridtjof Nansens Fond.

[36] O. Ruff and E. Ascher: Z. anorg. allgem. Chem., **185**, 369 (1929).

if the precipitate was kept under the mother liquor until no further change took place. On the other hand, if both compounds are slightly soluble, as in the case of $BaSO_4 - PbSO_4$ both cations are always present in the precipitate. From the analytical point of view, it is highly desirable to obtain more information regarding the ratio in which the two constituents occur in mixed crystals if precipitated under various conditions, and also of the stability of the crystals if kept under the mother liquor. Such studies are being made in our laboratory. It seems that mixed crystal formation is not materially dependent upon the manner of precipitation; i. e. whether an excess of cations or anions is present during the precipitation. This is in striking contrast to what occurs in "real coprecipitation," where the amount of coprecipitated foreign ions is highly dependent upon the conditions of precipitation.

Otto Hahn[37] formulates his precipitation rule in the following way; "An ion precipitates from any dilution with a precipitate crystallizing out, if it is incorporated in the crystal lattice; i.e. if it forms mixed crystals with ions of the crystalline precipitate. If it does not form mixed crystals, the ion remains in the filtrate even if its compound with ions of opposite charge in the precipitate is slightly soluble." According to O. Hahn[38] mixed crystal formation is possible even if it does not occur under normal conditions. This phenomenon is called "isodimorphism" and occurs for example according to Hahn[39] in the cases $BaCl_2 + RaB(ThB)$ or $RaD(ThD)$; $PbSO_4$ (ThB) $+ K_2SO_4$; $Tl_2SO_4 + ThBSO_4$; $PbCrO_4(ThB) + Ag_2CrO_4$. Although Hahn worked under unusual conditions (the concentration of the radioactive constituent always was extremely small) it seems to the author that Hahn has not proved definitely the ex'stence of such isodimorphism. Hahn as we will see later, does not make a distinction between mixed crystal formation and real coprecipitation, and there are reasons to assume that his cases of isodimorphism actually are examples of true coprecipitation. However, more experimental work must be done before a decision can be reached. From the above short discussion, it follows that in all cases of coprecipitation, the possibility of mixed crystal formation should be considered.

Adsorption and "Real Coprecipitation": In a study of the purity of precipitates, a distinction must be made between adsorption and real coprecipitation. If a precipitate separates as a flocculated colloid, it has a layer of flocculating ions rigidly adsorbed at its surface. These adsorbed ions can be partly removed by washing out or replaced by washing with suitable electrolyte solutions which do not interfere later in the analytical process (in gravimetric analysis: ammonium salts, acids and other electrolytes which volatilize on gentle ignition may be used.) If a real coprecipitation takes place, the impurities are present in the interior of the crystal and cannot be removed by a washing procedure. If a precipitate separates

[37] Otto Hahn: O. Erzbacher and N. Feichtinger: Ber., **59**, 2014 (1926); O. Hahn: Natur-wissenschaften, **14**, 1196 (1926).

[38] O. Hahn: Z. angew. Chem., **43**, 871 (1930).

[39] O. Hahn: Sitzungsber. preuss. Akad. Wiss., Physik. Math. Abt., **30**, 547 (1930).

in a micro crystalline form, such a coprecipitation always seems to occur even if there is no trace of mixed crystal formation. From scant data in the literature, and our own experience, one would infer that *colloidal precipitates always are contaminated by adsorbed ions but never contain the foreign ions in the interior of the particles.* In order to explain this, one has to realize that as long as the particle is in a colloidal state, the adsorbed foreign ions are present on the mobile side of the electrical double layer around the particle; they are not fixed at the surface. Therefore, as long as the particles are in the colloidal state, there is no reason why these ions which have retained their mobility should be incorporated during the growth of the particles (unless mixed crystal formation occurs). Here the electrokinetic potential of the particles is the governing factor. After the colloidal state has been passed, the thermodynamic potential is the main factor in the occlusion during the growth. As has been discussed in the first chapter, a crystal surface of a slightly soluble compound adsorbs that one of its own ions which happens to be in excess in the solution. A growing barium sulfate crystal for example, in the presence of a large excess of barium chloride in solution, will adsorb barium ions at its surface. Owing to the electroneutrality of both phases, the other ions of the electrolyte (here chloride ions) must be dragged along with the barium ions to the surface of the growing particle, where they will be more or less fixed. If the conditions are such that the crystals will grow very slowly, the chloride ions will be replaced more or less by sulfate ions, which fit in the crystal lattice and the coprecipitation will be relatively small. If the crystals grow much faster, there is no time available for a complete exchange between contaminating ions and those belonging to the crystal and a large coprecipitation will result. If finally, the conditions are such that owing to an extremely large supersaturation the particles are not given a chance to grow to bigger crystals, a flocculent colloid will separate and the coprecipitation will be extremely or negligibly small. Various studies made in our laboratory, which will be discussed in subsequent papers, yield results in complete harmony with the postulates of the developed theory. In the cases of calcium oxalate (E. B. Sandell) and barium sulfate, the largest coprecipitation is observed if the crystals are allowed to form under such conditions that they have a relatively large size. If the supersaturation is made so large that a flocculated colloid settles out, no coprecipitation should be observed but the impurities should be kept in an adsorbed state at the surface. If these small particles are allowed to recrystallize, a very slow growth takes place and a practically pure precipitate is obtained. If, finally, the conditions of precipitation are such that the crystals acquire an intermediate size, a real coprecipitation takes place. We therefore, arrive at the interesting conclusion that the largest crystals are the least pure if formed under analytical conditions. This is not in harmony with the general rules of analytical chemistry, where the directions usually are based on the assumption that larger crystals are purer than small crystals. In a recent publication, O. Hahn[38] expresses this rule in the following way:

"Für die analytische Chemie ergibt sich auch aus diesen Versuchen das ja schon in der Praxis verwendete Verfahren, Niederschläge in möglichst oberflächenarmer, gut kristallisierender und daher gut filtrierbarer Form auszuführen. *Alle Adsorptionsvorgänge werden dadurch stark zurückgedrängt.* Je mehr man von diesem Grundsatz abgeht, destomehr entfernt man sich von der Arbeitsweise des Analytikers; man kommt in das Gebiet des Kolloidchemikers; die Vorgänge an die Grenzflächen werden ausschlaggebend."

The contradiction between Hahn's and our views is explained by the fact that Hahn considers only *the adsorption at the surface after the crystals have been formed, but not the adsorption during the growth. For the study of coprecipitation the adsorption during the growth however is the predominating factor.* It is of interest to discuss a few other consequences of our picture of coprecipitation, although a more detailed discussion will be given later in connection with reports of practical work. The thermodynamic potential is determinative for the kind of adsorption taking place during the growth. If barium sulfate is precipitated from a solution containing an excess of sulfate ions, the latter will be adsorbed during the growth of the precipitate and drag *foreign cations* like H_3O^+; K^+, Na^+, Ca^{++} etc. to the surface; if on the other hand, barium ions are in excess during the growth, foreign anions like chloride, nitrate, etc. will be adsorbed and will coprecipitate with barium sulfate. *Depending upon the conditions of precipitation, a cation or anion occlusion will be predominant.* Experimentally, this has been shown to be true in the cases of barium sulfate and calcium oxalate monohydrate, although it should be mentioned that on account of incomplete dissociation of binary and ternary electrolytes, an apparent cation precipitation may be found where only anion coprecipitation is expected and also the reverse. However, in its general form, the rule derived seems to be of general applicability. Of special interest is the coprecipitation of ferric iron with barium sulfate. If the precipitation is carried out in a solution containing an excess of sulfate, a large coprecipitation of ferric iron—either as ferric ions or more probably as positive colloidal hydrous ferric oxide which is formed by hydrolysis— takes place. If the acidity of the solution is increased, the concentration of positive ferric oxide particles decreases and therefore, the amount coprecipitated also. On the other hand, if barium sulfate is precipitated from a solution containing an excess of barium ions, there is no coprecipitation of ferric iron at all.

According to the above views contaminating ions are not present *in* the crystal lattice, but as imperfections of the crystal lattice. They may be identified with the "Lockerstellen" or Hohlräume" in real crystals according to A. Smekal[40] or "centra of activity," according to H. S. Taylor.[41]

It should be remembered that coprecipitated foreign ions are not fixed by the lattice and therefore, keep more or less of their water of hydration. In this way the presence of the solvent (mother liquor) is explained and it

[40] A. Smekal: Z. angew. Chem., **42**, 489 (1929), where also other literature is given; comp. also W. Jost: Z. physik. Chem., **6B**, 88 (1929); **7**, 234 (1930).

[41] H. S. Taylor: Proc. Roy. Soc., **108**, 105 (1925).

is a problem of interest to determine whether there is a simple relation between the size of coprecipitated ions (which determines with the charge, the polarizing effect upon the solvent) on the one hand, and the ratio of amounts of coprecipitated ions and solvent on the other.

It is a well known fact that "real crystals" are far from ideal (Smekal);[40] they seem to have a porous structure. The more they are contaminated, the more pronounced the porous structure will be and vice versa. This may explain the peculiar fact that if a freshly formed precipitate is kept under the mother liquor, under such conditions that no recrystallization can take place, the amount of coprecipitated impurities decreases on aging and reaches a minimum after a day or so standing. This phenomenon seems to be quite general and has been noticed in the case of barium sulfate, lead sulfate, calcium oxalate, etc. The crystals seem to exert an action tending to perfect their own lattice which can be done only by expelling the impurities. In the interpretation of the peculiar aging effect, it should not be overlooked that in various cases a possibility of the primary formation of a metastable modification of the precipitate exists, which on standing may change into the stable modification thus yielding a radical internal change.

Summarizing then, it seems that real coprecipitation must be attributed to and is governed by adsorption phenomena during the growth of the crystals. A purely chemical interpretation based on the formation of definite chemical compounds between ions belonging to the lattice and contaminating ions of opposite sign, as is still done by Z. Karaoglanow[42] must be rejected.

D. Balarew[43] in his extensive studies on purity of precipitates, attributes *any* kind of coprecipitation to inner adsorption by crystalline salts. In so far as true coprecipitation is concerned, Balarew's views approach those developed in this paper; however, his picture and many of his statements are vague and he does not mention any connection between thermodynamic potential and kind of ion coprecipitation. As a result of coprecipitation "polar adsorption compounds" like $BaSO_4$, K_2SO_4, H_2O are formed according to Balarew. According to his opinion the occluded water still has solvent properties, but only for one special salt. If, for example, potassium sulfate and water are occluded by barium sulfate, no sodium or lithium sulfate can be coprecipitated, because the occluded water has solvent properties only for potassium sulfate. This view cannot be accepted as true, and is contrary to experimental evidence available at the present time. Although Balarew's papers contain many interesting data, his picture of coprecipitation is not of wide bearing and general applicability.

Ruff's work[44] on fractional precipitation, formation of mixed crystals and adsorption compounds is very important and stimulating, but again no

[42] Z. Karaoglanow: Ber., **63**, 597 (1930); Karaoglanow and B. Sargotschev: Z. anal. Chem., **187**, 273 (1930); **81**, 275 (1930); Z. anorg. allgem. Chem., **194**, 151 (1930); **195**, 105 (1931).

[43] Comp. summary of his work Kolloidchem. Beihefte, **30**, 249 (1930).

[44] O. Ruff and B. Hirsch: Z. anorg. allgem. Chem., **146**, 388; **150**, 85 (1925); **151**, 81 (1926); O. Ruff and E. Ascher: **185**, 369 (1929); O. Ruff: **185**, 387 (1929).

clear picture is developed for the case of true coprecipitation; especially adsorption during the growth of the crystals is not considered. For a quantitative treatment of the problem, the change of adsorption with time has to be studied more closely. Interesting and promising investigations of this subject are being carried out in O. Hahn's laboratory, especially by L. Imre.[45]

Moreover, the change in internal structure of a fresh precipitate in contact with its mother liquor has to be considered with regard to decrease of coprecipitated impurities on standing.

Summary

(1). Impurities in crystalline precipitates are due to coprecipitation or post precipitation. Three cases of coprecipitation are to be distinguished; Mixed crystal formation, in which the impurity is incorporated in the crystal lattice; real coprecipitation, in which impurities form imperfections in the crystal and surface adsorption by the precipitate after it is formed. In all these cases the presence of impurities is attributed to adsorption, either during the growth of the crystals or after their separation.

(2). In the case of real coprecipitation, the adsorption of foreign ions during the growth of the particles is of primary importance. Depending upon the thermodynamic potential of the precipitate during the growth, a cation or anion coprecipitation may be expected. If, for example, during the precipitation of barium sulfate, an excess of barium ions is present, a coprecipitation of anions may be expected, in the reverse case a coprecipitation of foreign cations.

(3). Up to a certain limit, coprecipitation with *a slightly* soluble substance increases with crystal size; a statement which is contrary to the general rules of analytical chemistry.

(4). The Paneth-Fajans precipitation rule should be extended in the following way: The higher the valence of an ion the more preferential it will be adsorbed by an ionic lattice which contains an excess of lattice ions of the sign opposite to that of the secondary adsorbed ions.

(5). A precipitate which does not exceed the colloidal dimensions contains impurities in an adsorbed but not in a coprecipitated state (provided there is no mixed crystal formation). As long as the particles are in colloidal solution, the foreign ions are present on the mobile side of the double layer and are not occluded.

(6). The analytical significance of the relation between particle size and solubility has been discussed. The concept of supersaturation with regard to speed of formation of precipitates has no exact significance; it depends upon size and surface tension of the tiny particles. Also for this reason von Weimarn's expression of the relation between the speed of formation of precipitates and supersaturation has no general validity.

[45] L. Imre: Z. angew. Chem., **43**, 875 (1930); Z. physik. Chem., **153A**, 127, 262 (1931).

(7). A discussion is given of filterability and properties of a flocculated colloid.

(8). An explanation is given of the fact observed by Dundon, that a mixture of very small and large crystals shows the normal solubility.

(9). The expression "amorphous modification" has no exact significance. The properties of an amorphous substance are more of less accidental; the mass action law cannot be applied when amorphous precipitates are dealt with.

(10). A freshly formed precipitate is not in equilibrium with its mother liquor. On standing, a change of the internal structure of the crystal takes place. Under any conditions, the amount of coprecipitated ions decreases with time of standing before filtration.

School of Chemistry of
The University of Minnesota,
Minneapolis, September. 1931.

SOME HEAT-CAPACITY DATA ON ORGANIC COMPOUNDS, OBTAINED WITH A RADIATION CALORIMETER

BY MONROE E. SPAGHT, S. BENSON THOMAS,[1] AND GEORGE S. PARKS

In a recent publication from this laboratory by Thomas and Parks,[2] in which specific heat data on boron trioxide glass were presented, a so-called "radiation" calorimeter was described. In order to obtain thermal data at higher temperatures on some organic compounds which have already been investigated at low temperatures by Parks, Huffman and their co-workers,[3] this apparatus has now been used for the measurement of the heat capacities and heats of fusion of the following nine substances: pentacosane, tritriacontane, hexamethylbenzene, diphenyl, triphenylmethane, naphthalene, dibenzoylethane, erythritol and mannitol. In addition some data have been obtained on liquid ethylbenzene and on ethyl azoxybenzoate, the latter being a substance that exists as a liquid-crystal within the temperature range $113.7°-122.5°C$.

Method

The apparatus used consists of a calorimeter suspended in air within a heavy copper jacket. This jacket is maintained at a given temperature difference (constant to $\pm 0.01°$) with respect to the calorimeter by means of a differential thermocouple, used in conjunction with an appropriate potentiometer, galvanometer and photoelectric relay-system. The rate of heat exchange between the calorimeter and its surrounding jacket at any instant is a function of the two temperatures involved. Thus,

$$q = K_T (T_J - T_C), \tag{1}$$

where q is the number of calories flowing from the jacket to the calorimeter per minute, T_J and T_C are the respective temperatures of the jacket and calorimeter, and K_T is the constant for Newton's law of cooling at the particular temperatures involved. We may also write the equation,

$$q = C_p \frac{dT_C}{dt}, \tag{2}$$

where C_p is the heat capacity of the calorimeter and contents and dT_C/dt is the rate of change of the temperature of the calorimeter per minute. Combining Equations 1 and 2 we then obtain,

$$C_p \frac{dT_C}{dt} = K_T (T_J - T_C). \tag{3}$$

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[1] Holder of the Shell Research Fellowship at Stanford University for the scholastic year 1930-31.

[2] Thomas and Parks: J. Phys. Chem., **35**, 2091 (1931).

[3] Parks, Huffman and Thomas: J. Am. Chem. Soc., **52**, 1032; Huffman, Parks and Daniels: 1547 (1930); Parks and Anderson: **48**, 1506 (1926).

If the rate dT_C/dt is first determined when the calorimeter is filled with a material of known heat capacity (in this case various weights of metallic copper and water), the constant K_T may be evaluated for a range of calorimeter temperatures. Then, in turn, the heat capacities of the calorimeter and a second substance may be determined by measuring the corresponding values of dT_C/dt when the calorimeter is filled with this substance. As the heat capacity of the calorimeter itself is known, the specific heat of the second substance can be readily calculated.

Heats of fusion and transition may be determined by summing up the total heat input to the calorimeter as its temperature is raised from a point T_1, just below the region of premelting, to a point T_2, slightly above the melting point, and then subtracting the heat necessary to raise the temperature of the calorimeter and contents from T_1 to the melting point and from the melting point to T_2. These latter quantities are calculated from the extrapolated specific heat curves.

Thus,

$$\triangle H_{fusion} = \int_{T_1}^{T_2} K_T \, (T_J - T_C)dt \; - \; \int_{T_1}^{T_2} C_p \, dT \tag{4}$$

where $\triangle H_{fusion}$ is the heat of fusion of the given sample and C_p is the total heat capacity of the calorimeter and contents.

Materials

Pentacosane and Tritriacontane.—These were fractions of paraffin wax, prepared in the Research Laboratory of the Standard Oil Company of Indiana.[1] Each sample was recrystallized three times from ethylene dichloride in our own laboratory. The melting points were: pentacosane, 53.4°; and tritriacontane, 71.0°C.

Ethylbenzene.—This compound was synthesized by the Friedel-Crafts reaction in the Chemical Laboratory of Johns Hopkins University. It was purified by three fractional distillations. The final product boiled at 135.6° and melted sharply at −95.1°C.

Hexamethylbenzene, Diphenyl and Triphenylmethane.—These were relatively pure compounds obtained from the Eastman Kodak Company. In all cases they were subjected to two or more fractional crystallizations from ethyl alcohol. The melting points of the final products were found to be: hexamethylbenzene, 165.5°; diphenyl, 68.3°; and triphenylmethane, 92.1°C.

Naphthalene.—Kahlbaum's naphthalene was subjected to four fractional distillations. The unusually sharp melting curve shown by this material indicated that it was very pure.

Dibenzoylethane.—This sample (melting point 145.4°C) was supplied to us in pure form by Professor Conant[2] of Harvard University.

[1] Buchler and Graves: Ind. Eng. Chem., 19, 718 (1927).
[2] Conant and Lutz: J. Am. Chem. Soc., 45, 1303 (1923).

Erythritol and Mannitol.—C. P. Pfanstiehl products with melting points of 118.4° and 166.0°C, respectively, were used without further purification.

Ethyl azoxybenzoate.—A very pure sample of this substance was kindly loaned to us by Professor J. W. McBain. In our experiments we found the following melting points: *crystalline solid to liquid-crystal* 113.7°; and *liquid-crystal to liquid,* 122.5°C.

Experimental Results

Table I presents specific heat data for the solid and liquid states of the several compounds investigated (save ethylbenzene). In each case a large number of individual determinations (fifty to one hundred) of the specific heats were made. From a plot of these results a smooth curve was then constructed, and from this the values given in the table were taken. In no case were the actual experimental points more than two per cent off this curve. The absolute accuracy of the tabulated mean values is believed to be within three per cent.

Table I

Specific Heat Data
(in calories per gram)

Temp. °C	Naphthalene Crystals	Hexamethyl-benzene Crystals	Erythritol Crystals	Mannitol Crystals	Dibenzoyl-ethane Crystals
30	.315	.380	.334	.321	.303
40	.332	.393	.345	.331	.313
50	.350	.407	.357	.341	.323
60	.367	.420	.370	.352	.333
70	.385	.434	.383	.363	.344
80	*M.P. 79.9°C*	.448	.396	.373	.354
90	.424	.463	.408	.384	.364
100	.432	.478	.421	.394	.374
		Transition			
110	.440	*110.6°*	.434	.404	.384
120	.447	.466	*M.P. 118.4°*	.415	.395
130	.455	.480	.683	.425	.405
140	.462	.493	:688	.435	*M.P. 145.4*
150	.470	.507	.693	.446	.506
160	.477	*M.P. 165.5*		.456	.509
170	.485	.555		*M.P. 166.0°*	.512
180	.493	.566		.720	.515
190	.500	.576		.721	.518
200		.587		.723 ·	

TABLE I (Continued)

Temp. °C	Ethyl-Azoxybenzoate Crystals	Triphenyl-methane Crystals	Diphenyl Crystals	Pentacosane Crystals	Tritriacontane Crystals
30	.315	.302	.307	.453	.464
40	.326	.314	.320	.468	.483
50	.337	.328	.333	$M.P.\ 53.4°$	.501
60	.348	.342	.345	.553	.520
70	.358	.355	$M.P.\ 68.3°$	.561	$M.P.\ 71.0°$
80	.369	.368	.422	.569	.572
90	.380	$M.P.\ 92.1°$	.430	.578	.579
100	.391	.442	.438	.586	.586
110	.401	.449			.592
	1st M.P. 113.7°				
116.2	.471				
120	*2nd M.P. 122.5°*	.456			
130	.472				
140	.475				
150	.478				

As an example of the results obtained, we have plotted our specific heat curves for solid and liquid naphthalene (Fig. 1) together with the values reported by Battelli,[1] Schlamp,[2] and Andrews.[3] Being stable and easily purified, naphthalene serves as an excellent reference substance with which the results of different calorimetric methods may be compared.

The specific heat data given for the solid states of pentacosane and tritriacontane were not determined in this investigation (because of the premelting which occurred within the temperature range studied), but were obtained by extrapolation of the low temperature results published by Parks, Huffman and Thomas.[4] The values given for the liquid states of these compounds are those found in this investigation.

Using a special adiabatic calorimeter Williams and Daniels[5] found an irregular curve for the heat capacity of liquid ethylbenzene in the temperature range 20°–40°C. Measurements made for the purpose of investigating this reported irregularity show a perfectly smooth curve from 5° to 60°C. The actual values obtained check closely with those of Huffman, Parks, and Daniels,[6] who previously worked on the same material.

[1] Battelli: Atti. del reale instituto Veneto di scienze, lettere ed arti, **3**, 1781 (1884).

[2] Schlamp: Ber. Oberhess. Ges. f. Naturw. u. Heilk., **31**, 100 (1895).

[3] Andrews, Lynn and Johnston: J. Am. Chem. Soc., **48**, 1274 (1926).

[4] Parks, Huffman and Thomas: J. Am. Chem. Soc., **52**, 1032 (1930).

[5] Williams and Daniels: J. Am. Chem. Soc., **46**, 1569 (1924).

[6] Huffman, Parks and Daniels: J. Am. Chem. Soc., **52**, 1547 (1930).
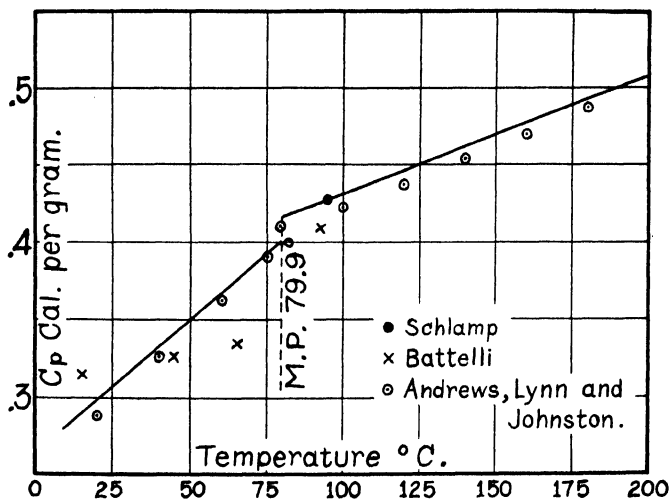
FIG. 1

Specific heat curves for crystalline and liquid naphthalene

The heats of fusion determined for the several compounds are presented in Table II.

TABLE II

Fusion and Transition Data

Substance	Nature of change	Temperature l°C	Heat effect (cal. per gram)
Pentacosane	Fusion	53.4	53.8
Tritriacontane	”	71.0	54.0
Hexamethylbenzene	Transition	110.6	2.6
”	Fusion	165.5	30.4
Diphenyl	”	68.3	28.9
Triphenylmethane	”	92.1	21.5
Naphthalene	”	79.9	35.8
Dibenzoylethane	”	145.4	39.1
Erythritol	”	118.4	82.9
Mannitol	”	166.0	70.3
Ethyl azoxybenzoate	1st fusion	113.7	14.3
”	2nd ”	122.5	3.8

The results for pentacosane and tritriacontane, 53.8 and 54.0 calories per gram, respectively, are in very good agreement with the corresponding values of 53.5 and 54.0 calories per gram obtained by Parks and Todd,[1] who used a method of mixtures. The value of 28.9 calories per gram found for diphenyl is in close agreement with that of Eykmann[2] (28.5 calories). The heat of fusion of triphenylmethane was found to be 21.5 calories per gram. This

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[1] Parks and Todd: Ind. Eng. Chem., 21, 1235 (1929).

[2] Eykmann: Z. physik. Chem., 4, 518 (1889).
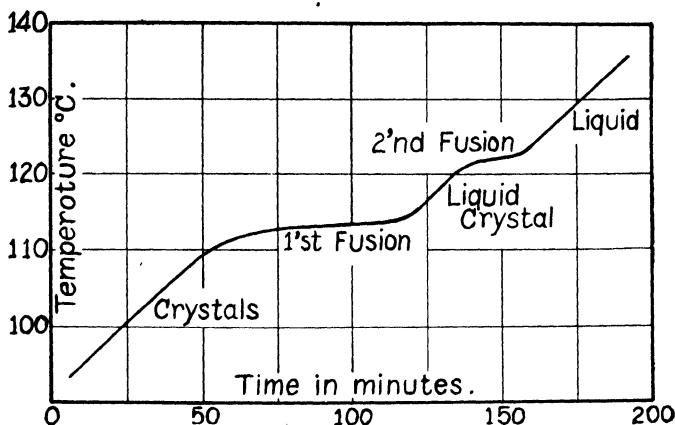
FIG. 2

Time-temperature curve of ethyl azoxybenzoate

is considerably higher than the value (17.8 calories) obtained by Hildebrand and his co-workers.[1] Their value, however, is probably low, owing to an inadequate allowance for the premelting of the sample.

Hexamethylbenzene is of particular interest in that it undergoes a sharp crystalline transition at 110.6°C. The heat of this transition was found to be 2.6 cal. per gram. It appears that hexamethylbenzene is unusually prone to undergo crystalline changes, as Huffman, Parks, and Daniels previously found a similar transition at −165°C, which involved a heat effect of 1.5 cal. per gram.
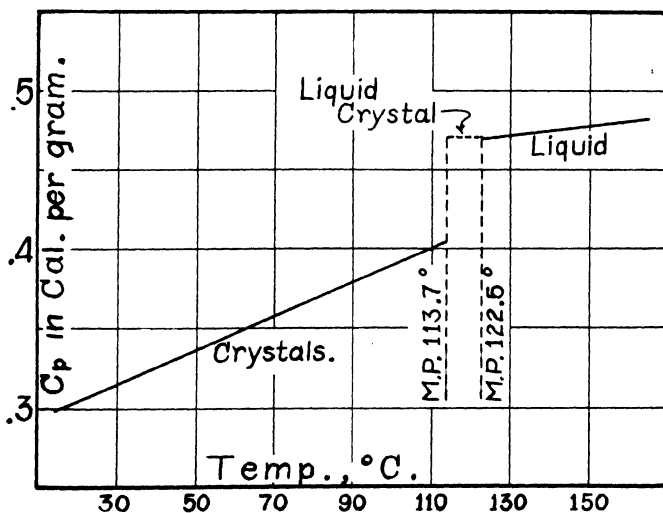
FIG. 3

The specific heat curves for the three states of ethyl azoxybenzoate

[1] Hildebrand, Duschak, Foster and Beebe: J. Am. Chem. Soc., 39, 2293 (1917).

The heat of fusion of naphthalene is generally accepted as being close to 35.6 cal. per gram. The value of 35.8 obtained in this investigation thus agrees as well as can be expected, considering the limitations of the method employed.

The two heats of fusion of ethyl azoxybenzoate represent the heat effect accompanying the transition from the solid state to an anisotropic liquid or liquid-crystal, 113.7°C, and that from the liquid-crystal state to the true isotropic liquid, 122.5°C. Very little accurate thermal data have been obtained for liquid crystals, but our results are in general agreement with other direct measurements made on such compounds as well as with the values calculated from cryoscopic data.[1]

The thermal properties of substances that undergo complicated transitions are frequently more clearly shown by time-temperature curves than by the corresponding heat capacities and heats of fusion. Accordingly, in Fig. 2 we have shown the time-temperature curve for ethyl azoxybenzoate as it is slowly heated from the solid to the liquid-crystalline and true liquid states. Fig. 3, which is in effect derived from Fig. 2, presents the heat capacity curves for the three states. The single value calculated for the specific heat of the liquid-crystal is probably somewhat high, due to the close proximity of the two transition stages.

Summary

1. By use of a "radiation" calorimeter, the heats of fusion of nine organic compounds have been determined and the heat capacities of these substances have been measured in both the solid and liquid states.

2. A short series of measurements on liquid ethylbenzene shows no evidence of previously reported irregularities in the heat capacity curve.

3. Ethyl azoxybenzoate, a substance showing the liquid-crystal phenomenon, has been investigated over the temperature range 30°–150°C.

Department of Chemistry,
Stanford University, California.
October 27, 1931.

[1] For other data regarding heat effects with liquid crystals see: Dr. Rudolf Schenck: "Kristallinische Flüssigkeiten und flüssige Kristalle," 84 (1905); Amerio: Nuovo Cimento (5), Vol. 2, Nov. Dec. 1901; Hulett: Z. physik. Chem., 28, 645 (1899); Schenck: Z. physik. Chem., 28, 285 (1899).

THE ACTION OF MOLECULAR NITROGEN
ON HIGHLY PURIFIED IRON

BY H. H. GRAY AND M. B. THOMPSON

Introductory

The object of the following account of experimental work is two-fold in that, primarily, it forms part of an attempt to separate the factors concerned in the previously published account of the remarkable effect of nitrogen on the solubility and carbon content of ferrous alloys which have been heated in an atmosphere of molecular nitrogen;[1] secondly it seems advisable to produce evidence which shall definitely establish the fact that molecular nitrogen reacts readily with highly purified iron, irrespective of whether the iron is in the alpha- or the gamma-form. In spite of the fact that many workers have reported the action of molecular nitrogen on iron and that the results obtained by the present writers[2] leave no doubt that nitrogen (as distinct from ammonia) readily reacts with iron and that these results were confirmed by analytical determinations, solution tests and microscopical examination, there still exists the impression amongst scientific and technical investigators that molecular nitrogen does not combine with iron. For instance, Emmett, Hendricks and Brunauer[3] in an important paper state that "Bauer and Voerman, Maxted and others tried without success to form iron nitride by the action of nitrogen at pressures as high as 200 atmospheres on iron between temperatures of 400°C and 700°C."

The context, combined with the rather limited list of references, is a clear indication that these workers are under the impression that nitrogen and iron do not react when the nitrogen is presented to the iron in the elementary form. Had it been implied, as it is in the paper of Noyes and Smith[4] that the action of molecular nitrogen on iron is not a suitable method for the preparation of iron nitride in quantity, then it would have been possible to agree with the inference; but to imply that even at 200 atmospheres elementary nitrogen does not unite with iron at temperatures between 400° and 700°C seems to the present writers to contradict weighty and well-attested evidence and to render all the more advisable the publication of such experimental facts as follow herein.

Again, in a very recent paper[5] Brunauer, Jefferson, Emmett and Hendricks use elementary nitrogen to wash out an apparatus containing heated iron and iron nitride on the understanding that the nitrogen in this form is inert.

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[1] Gray: J. Soc. Chem. Ind., 45, 365-366 T (1926); Gray and Thompson: 48, 21-28 T; 50, 353-357 T.

[2] Loc. cit.

[3] J. Am. Chem. Soc., 52, 1456 (1930).

[4] J. Am. Chem. Soc., 43, 475 (1921).

[5] J. Am. Chem. Soc., 53, 1778 (1931).

The advisability of coming to a definite conclusion with regard to the question of the possibility of elementary nitrogen reacting with ferrous materials is of importance in connection with the mechanism of the ammonia synthesis by the agency of iron catalysts; the explanations put forward by W. A. Bone and his co-workers for the delaying effect of nitrogen in high pressure explosions, first recorded by Bone, Gray and Dawson;[1] the dissociation pressures of the iron nitrides; the occurrence of nitrogen in steel made by the Bessemer process. In all these matters, which are of considerable interest and importance, there is the possibility of further light being thrown on the theoretical side by taking into consideration the chemical activity of ordinary elementary nitrogen as shown in the experiments here recorded.

Experimental

The general method of experimentation was to heat the moderately polished specimen of iron for five hours in highly purified nitrogen in an electric tube furnace. The details of the furnace, nitrogen preparation and purification have been given in previous papers.[2] The only modification introduced was the substitution of a fused transparent silica tube for the vitreosil tube when vacuum experiments were carried out. The apparatus was then an 'all vitreous' one, the silica tube being connected to the glass part of the apparatus by means of ground glass caps. A slow stream of nitrogen was maintained throughout the whole of the apparatus during the experiments (except in vacuum experiments) and specimens were allowed to cool in contact with pure dry nitrogen.

The vacuum was obtained (after baking the tube at 300°) by means of a hand-worked Töpler pump. The apparatus was considered to be satisfactorily evacuated when after standing over-night under vacuum, no more gas could be collected from it. A slow-acting pump, fitted with a gas collecting apparatus, was found to be advantageous in dealing with the de-gassing experiments since it enabled the experimenter to follow visually the progress of the de-gassing and rendered improbable any premature conclusions as to the completeness, at any given time, of the vacuum inside the apparatus. Even the slowest acting pump was found capable of evacuating the apparatus much more rapidly than the gas was given up from the iron towards the end of a de-gasification. Complete de-gasification was denoted by the cessation of gas evolution.

Nitrogen Estimation

Nitrogen was estimated as ammonia. The metal, after nitrogenation, was immersed and dissolved in hot concentrated hydrochloric acid the use of which was rendered necessary by the effect of the nitrogenation on the solubility of the iron; (un-nitrogenated iron dissolved readily in dilute hydrochloric acid).

[1] Phil. Trans. Roy. Soc., 215A, 275-318.
[2] Loc. cit.

This solution was then distilled with caustic alkali and the distillate collected in very dilute sulphuric acid. The distillate was then treated with Nessler's solution in the ordinary way. Every determination was rigidly controlled by duplicate blank determinations and was carried out in an ammonia-free atmosphere.

Purified Iron

(a) *Iron Powder.*

This was prepared by dissolving purified ferrous ammonium sulphate in distilled water, oxidising the solution with nitric acid, precipitating the ferric hydroxide with ammonia and washing by decantation the precipitated ferric hydroxide until the washings gave a negative test for sulphuric acid. The dried ferric hydroxide was then reduced in hydrogen and cooled in hydrogen. The reduced powder was not pyrophoric and was de-hydrogenated in vacuo before being nitrogenated.

(b) *Electrolytic Iron Flakes.*

Ferrous ammonium oxalate solution was electrolysed with all the precautions and in the manner recommended by Classen in "Quantitative Analysis by Electrolysis." In order to obtain the iron in very thin flakes (calculated by us to be 0.0003 cm. in thickness) the iron was deposited on one side of a cylinder of thin sheet aluminium: the aluminium was then dissolved off by concentrated caustic potash, leaving the electrolytic iron in the form of clean lustrous flakes.

These flakes were washed in distilled water, dried and stored in water-free alcohol which had been dried by several distillations over glycerol. Before use, flakes were removed from the alcohol, washed with dry ether and dried at 100° C.

(c) *Iron Electrodes.*

Since neither powder nor flakes were found suitable for microscopic examination, another form of highly purified 'massive' iron was sought for and found in the electrodes supplied by Messrs. Adam Hilger from the collection of Sir William Crookes. These electrodes have served other investigators as sources of purified iron and have the analysis:—

C. 0.01; Si trace; S. 0.029; P. 0.008; Mn. 0.025; Cu 0.033; Ni 0.006

Thus, about 99% of any polished surface prepared on such a piece of iron is presumably ferrite, and, as such, is eminently suited to demonstrate the action of molecular nitrogen on massive iron of high purity. It would be possible to devote considerable time and energy to the preparation of a massive specimen of pure iron without obtaining a sample of higher purity than the Crookes electrode.

Samples of the electrode to be nitrogenated were polished to a moderate degree by means of emery paper (finishing with 0000) before being inserted in the furnace. Such a surface under the microscope was structureless but not free from scratches. These scratches and their obliteration afforded a valuable guide to the examination of the fused layer formed during nitrogenation.

The Photographs

As most metallographic microphotographs are obtained as the result of differential attack by some corrosive liquid on the polished metal surface, it is advisable here to point out that unless otherwise stated our structures are produced without any such medium. The structures from which our conclusions are drawn are produced by the action of nitrogen gas on the metal surface and it is only where further information was desired that a liquid reagent (alcoholic picric acid) was used. Where this has been done the photograph will be described as one of an etched specimen, the original nitrogen structures being described as unetched.

Precautions against Oxygen

As detailed in previous publications[1] strict precautions were taken against the intrusion of oxygen into the reaction vessel and the consistency of our results is satisfactory evidence that oxygen was not present in the experiments quoted here and from which our conclusions are drawn. The precautions taken were of two kinds: (a) the nitrogen was purified; (b) the nitrogenated samples were protected by copper packings in the early parts of the reaction tube and were, in addition, wrapped in several thicknesses of iron gauze which were relied upon to intercept the minute traces of oxygen which might have eluded the original purification processes. In fact the experience gained early in the work showed clearly that a small amount of oxygen, although it could introduce confusion into the microscopic side of our work, interfered so drastically with the production of the insoluble layer caused by nitrogenation that not only had we to eliminate the oxygen in self defence but an unsatisfactory result was almost invariably an indication that the reaction tube was developing a crack. Furthermore in one or two cases of partially successful experiments where it was known that towards the end of the experiment air had leaked on to the specimen through a crack in the tube the oxide coating of various colours disappeared at once in the dilute hydrochloric acid. This was, of course, in marked contrast to the behaviour of the nitrogenated material in cases where there was every reason to suppose that oxygen had been successfully excluded.

Microscopic Evidence

Nitrogenation of Crookes electrode at various temperatures.

Nitrogenated at 500°C:—A grey film formed over the whole specimen. This film was interrupted by small black spots corresponding to the segregated areas to be expected from the known small amount of impurities present. (see analysis). Microscopic examination showed the film to have a granular structure and that the black spots had been the seat of marked gaseous action. No polygonal grain system had developed; the surface was dull and the capacity for reflecting light was not now so great as on the original un-nitrogenated specimen.

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[1] Loc. cit.

Etched with alcoholic picric acid:—The specimen etched very readily and stained considerably. The ready etching and the resulting stain are both quite characteristic of nitrogenation at temperatures below 700°C. The un-nitrogenated iron electrode neither etches readily nor does it stain.

Microscopic examination showed that a dark brown layer of granular structure had been formed over the main body of the specimen (which is ferrite) and that the localised impurities had been the scene of vigorous action. The black spots noticed before etching had now been converted into clear areas by the etching reagent and these clear areas showed widened grain walls strongly suggesting that the treatment received had resulted in the expulsion or extrusion through these grain walls of the products of the reaction. The main body of the specimen, that is, the ferrite, was thus clearly differentiated from the segregated impurities, small as these were in amount.

Nitrogenated at 700°C:—There was no grey film as at 500°C. Instead there was developed a small polygonal grain system with signs of double layer formation and accompanying glossiness. The grains are irregular in size.

Etched with alcoholic picric acid:—The specimen etched with a rapidity intermediate between that of the un-nitrogenated electrode and the one nitrogenated at 500°C. There was marked orientation as shown by differential attack of the different grains, some of the grains being so glassy as to have resisted the etchant almost entirely. The nitrogen attack would seem to have been markedly influenced by the orientation of the original ferrite grains as one would expect.

Nitrogenated at 750°C:—The surface was clean with well developed polygonal grain structure the grain walls of which were of the line type and straighter than those due to the original ferrite, (cf. vacuum experiment at 750°C.) Glassiness and double structure were well developed. There were very few bubbles.

Etched surface. The specimen etches with moderate rapidity but does not stain. The surface is seen to be covered almost entirely with dark granular material, the different densities of which on the separate grains produced a marked orientation effect. (The un-nitrogenated material gave no corresponding structure).

There are no prisms or secondary crystallisation effects in this case, the transparent crystalline layer being quite clear and homogeneous.

Nitrogenated at 1100°C:—At this temperature the specimen had a beautifully vitreous appearance due to the thicker layer of fused material. So marked was the capacity for reflecting light that the source of (vertical) illumination had to be drastically cut down in order to reduce the glare. This was one of the most noticeable features of the nitrogenated material as compared with the un-nitrogenated samples.

The walls of the polygonal grain system in this specimen are (in the main) not of the hair line type so noticeable in the photograph previously published by Gray and Thompson[1] but consist chiefly of long narrow crystals arranged end to end in a markedly linear manner. The rate of cooling would seem to

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[1] Loc. cit.

influence considerably the distribution between hair line or 'crack' boundaries and the boundaries made up of long crystals. Generally speaking the layer is seen to be under considerable stress due to crystallisation forces. The small crystalline nuclei, of which there are many, show definite alignment. Many fine wavy strain lines are to be seen at higher magnifications and these are possibly connected with the formation of the duplex structure which the crystalline layer proves to have on etching. At high magnifications bubbles are to be found imprisoned in the transparent layer.

Etched surface. The surface etches easily with a light brown stain. Etching developed a very coarse irregular structure the chief features of which were a dark brown background of duplex structure in which were embedded masses of a brilliant white material resembling ordinary massive cementite. The unusual ease with which this specimen etched is probably due to the very partial crystallisation causing metastability (from the point of view of crystallisation) and which is itself due to the relatively rapid rate of cooling.

Microscopic Features of Electrolytic Iron Flakes

Nitrogenated at 700°C:—As nitrogenated the flakes had a pewter-like appearance and had caked together. A microscopic examination of the unetched flakes revealed small polygonal glassy grains outlined by thick walls which showed a duplex structure.

Nitrogenated at 1100°C:—As nitrogenated the flakes showed the usual transparent layer with features of secondary crystallisation in the layer. The tendency to develop a duplex structure is much more marked in these electrolytic flakes than is the case with the 'massive' iron electrode and is to be interpreted as an indication that the original idea of making the flakes very thin has been partially successful. Owing to the fact that the iron is presented to the nitrogen in this very accessible form the nitrogen has been able to attack the iron to a greater extent than was possible in the massive form. The nitrogenation has thus gone further than is possible in the case of the massive specimens and the metastable transparent layer is being replaced by the ultimate form which the authors consider to be of a duplex nature. Experiments with other sheet material tend to confirm this view.

Iron Powder

When highly purified iron powder was nitrogenated it was found to have sintered together into a solid cake capable of being picked out of the boat by means of a pin. Although this material was not suitable either for microscopic work or for solution tests it was found by means of the microscope that the particles of iron were surrounded by a glossy fused mass and that the caked material was really a mass of separate particles cemented together by the transparent fused material. From visual observation under the microscope it may be said that the fused transparent material on the powder particles presented characteristics similar to those found on nitrogenated 'massive' iron (notably the entrapped bubbles).

Summary

Molecular nitrogen acts on purified iron at temperatures as low as 500°C (and from other evidence the temperature may be as low as 200°C) to form a grey film, which etches to show a duplex structure and which, at about 700°C gives place to a fused transparent layer. This transparent layer largely inhibits further action by the gaseous nitrogen but probably reacts with the underlying metal. This latter tendency is shown by the fact that the most obvious sign of the action of nitrogen on the ferrous material, namely the resistance to hydrochloric acid, has been shown in previous papers[1] not to be confined to the transparent layer of microscopic thickness but to extend to a depth of macroscopic dimensions. (Vide infra under Solution tests.)

It is probable that more extended experimental work would show that many of the phenomena noted in the work of A. Fry,[2] as being due to the action of ammonia can be repeated by means of molecular nitrogen. In this connection it should be noted that the nitrogenations carried out by us and described in this paper lasted for only 5 hours, a period of time quite insufficient to bring about the technical operation known as 'nitriding'. This operation, carried out by means of ammonia gas, seems to owe its penetrating power to the decomposition of the ammonia, an operation which would be very likely to provide the opening up of the metallic surface. In the case of molecular nitrogen there is neither decomposing ammonia nor hydrogen to help to break up the surface of the metal and so we get a smooth surface which tends to inhibit further action.

The Reality of the Nitrogen Effect
A Comparison between heating in a Vacuum and heating in Nitrogen

In order to prove the reality of the nitrogen effect and to show that it was neither a thermal nor an allotropic effect, and that in fact it was not an effect which could be produced in the absence of nitrogen, vacuum control experiments were carried out in which samples of Crookes electrode prepared under identical conditions were heated respectively in nitrogen and in a vacuum. The only difference between the treatment of the two specimens was that in the one case the heating was carried out in an atmosphere of nitrogen whilst in the other the sample was heated in the vacuum produced by means of a Töpler pump. The results show that the effect produced by heating in nitrogen could not be obtained by heating in a vacuum, and put beyond question the fact that molecular nitrogen does react with iron. This is not the same thing as saying that the action of molecular nitrogen is a method of preparing iron nitride. The use of ammonia seems to be advisable for this purpose and is indeed understandable on the basis that the decomposed ammonia and the decomposing ammonia tend to open up the metallic surface and render it susceptible to the attack of the gaseous atmosphere. Further, the observations of Maxted in "Ammonia and the Nitrides" make it clear that the pressure of the ammonia itself is a controlling factor in the formation of nitrides.

[1] Loc. cit.
[2] Stahl und Eisen, **43**, 1271.

Comparison between Nitrogen and Vacuum Experiments

Temperature 500°C

	Nitrogenated	Vacuum
As from the furnace.	A grey film covered the surface, obvious to the naked eye and showing under the microscope as a uniform granular coating.	Untarnished to the naked eye. Microscopic examination showed no film.
Etched with alcoholic picric acid.	Etched rapidly and stained dark. Microscopic examination showed the surface to be essentially of a dark bluish brown granular material.	Etches with difficulty. Does not stain. Microscopic examination revealed a surface essentially free from colour or granular material and quite different from the corresponding nitrogenated one.

Temperature 700°C

	Nitrogenated	Vacuum
As from the furnace.	Polygonal structure, glassiness and double structure all well developed. The surface showed definite signs of fusion and the partial obliteration of scratches. The specimen did not rust when left exposed to the atmosphere.	The surface was quite untarnished and the original polish was only slightly dulled to the naked eye. Under the microscope a polygonal grain structure could be detected such as would be of necessity developed by vacuum heating owing to the de-gassing. The surface is not glassy, shows no signs of fusion and the raised edges of the polygonal grains are precisely what would be expected if the gases expelled during heating had issued from the grain walls. There is a total dissimilarity between this surface and the corresponding one heated in nitrogen. This specimen rusted easily.
Etched with alcoholic picric acid.	The rate of etching was moderate. The grains etched differentially, showing marked orientation. The reflecting power was still considerable.	Etched rapidly and uniformly. The structure due to de-gassing was obliterated. No sign of differential etching was seen. The reflecting power of the surface was small.

Temperature 750°C

	Nitrogenated	Vacuum
As from the furnace.	The surface was clean with well developed polygonal grain system. The grain walls were markedly straight. Glassiness well developed owing to thin transparent layer. (See Fig. 2.)	The surface was clean and free from tarnish. The scratches purposely left on the original surface were much emphasised, which is precisely opposite to what occurs when such a surface is nitrogenated. The reflecting power was poor and under the microscope the usual faintly outlined grain structure due to degassing was seen. (See Fig. 1.)
Etched with alcoholic picric acid.	Etched fairly easily but did not stain. There was marked orientation of grain surface owing to differential nitrogen attack.	This specimen was not etched as it was required for other tests.
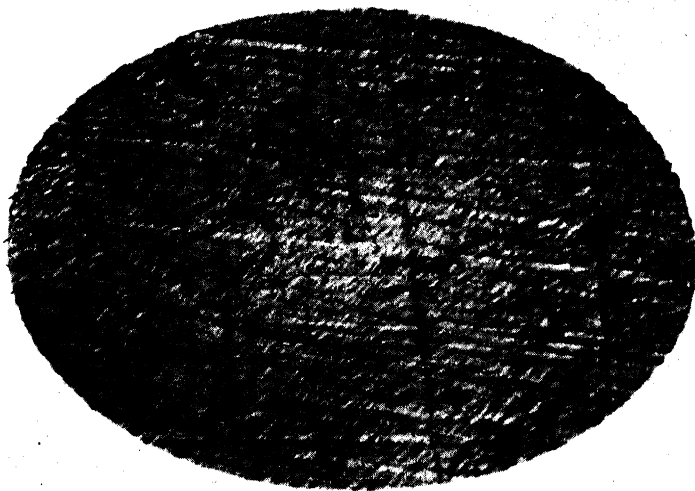
FIG. 1

Crookes electrode heated in vacuo at 750°C.   Unetched × 412.
Shows faint degassing structure. Original scratches emphasized.
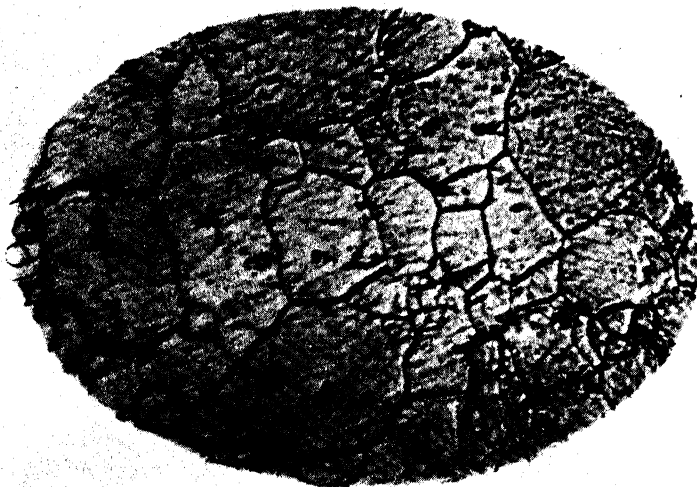
FIG. 2

Crookes electrode nitrogenated at 750°C. Unetched × 412. Shows the
early stages of the transparent layer. Original scratches obliterated.

Summary

In spite of the fact that, owing to the liberation of gas from the iron itself, it is not accurate to speak of a vacuum test in the case of iron heated in an evacuated vessel at temperatures of 700°C or so, our experiments, supplemented by photographic records, clearly prove that heating in nitrogen produces effects which are not produced when iron is heated in a vessel which is subjected to continuous evacuation by means of a hand-worked Töpler pump. In other words it is a fair inference that the nitrogen exerts a specific influence on the iron, this action being shown by the detailed changes in properties as tabulated above.

The structure produced by the degassing is easily distinguishable from that produced by nitrogenation.

Composition of the Crystalline Layer

Since the transparent crystalline layer obtained by the action of molecular nitrogen on purified iron is of microscopic dimensions it is clear that stoichiometric conclusions should be drawn only after very definite evidence has been accumulated. Our experience would lead to the conclusion that the matter would afford ample material for an extended and separate research. Indeed the results of our microscopic examination tend to the conclusion that the layer contains two constituents and that, given equilibrium conditions the duplex nature of the layer would be made clear. Such conclusions have not,

however, been definitely sought for present publication since their establishing would entail the command of experimental conditions not, as yet, available. The heating period of 5 hours is too short for equilibrium to be established in massive specimens.

Our analytical results (vide infra) show the absorption of small but definite amounts of nitrogen and the detection of these small amounts would seem to indicate the presence of nitride nitrogen. Since however, the question of the metallographic, as distinct from the chemical, composition of the layer is involved and since the possibility of solid solutions both of gas and of nitride must be considered it would seem to be unnecessary at this stage to do more than record the experimental facts. As an example of the difficulty may be quoted the fact that an X-ray examination failed to reveal nitrogen which our chemical analysis showed to be present. This experience is borne out by the similar results obtained by Brunauer, Jefferson, Emmett and Hendricks[1] when a nitrogen content of 0.17% gave an X-ray pattern showing no FeN but only Fe. This is an interesting case of the failure of a physical method to detect an amount of an impurity easily detectable by chemical means. Furthermore the work of J. H. Andrew,[2] and the history of the steel industry indicates quite plainly that such amounts as 0.17% of nitrogen and of the nitrogen family of elements are of major importance, even though the X-ray diffraction pattern gave no reliable sign of their presence.

Following are results obtained on the nitrogen content of various nitrogenated materials.

Iron Wire Gauze

This wire gauze had been used for wrapping round various samples of ferrous materials during nitrogenation; it had thus had at least 22 hours' treatment in nitrogen at 1000-1100°C. It was very brittle, dull grey in appearance. It was quite different in mechanical properties from the original gauze. The nitrogen added to the gauze was found to be 0.01%. *N. B. 5.*

Thin Sheet Iron

This material was thin sheet iron of high commercial purity which had been nitrogenated at 1000°C for 16 hours. At the end of that time the weight had become constant.

Nitrogen in nitrogenated material	0.013%
Nitrogen in original material	0.003%
Nitrogen added during nitrogenation	0.01 %

The above figures, whilst they indicate a positive absorption of nitrogen, are necessarily low since they are given in percentages and seeing that the phenomenon which was the subject of our investigation is chiefly noticeable from the point of view of the microscopic transparent layer it necessarily follows that a large proportion of the iron concerned in the percentage figure

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[1] J. Am. Chem. Soc., **53**, 1778 (1931).
[2] Iron Steel Inst., **1912 ii**, 210.

is not important in connection with the nitrogen which has taken part in the formation of the layer. In other words the figures must not be regarded as evidence either for or against the formation of iron nitride except insofar as the ammonia formed during the distillation is presumably due to nitride. The percentages then have no stoichiometric significance. They merely indicate that molecular nitrogen can combine with iron to form a transparent crystalline layer of, as yet, undetermined composition, either chemical or metallographic. The combination takes place independently of whether the iron is in the alpha or the gamma state.

Nitrogen found in "Ammonified" Crookes Electrode

In order to compare nitrogenation with ammonification a Crookes electrode was heated in ammonia gas at 1100°C, which temperature is far higher than the technical 'nitriding' temperature. This electrode was then treated with N/2 hydrochloric acid for 24 hours. The 'ammonified' electrode, in contradistinction to the nitrogenated electrodes, was easily attacked by acid of this concentration and the solution was found to contain ammonia to an extent which, when calculated on the total weight of the electrode amounted to 0.03% nitrogen. This corresponds to a nitrogen content of 0.5% in the dissolved portion of the electrode. This value of 0.5% is necessarily approximate owing to the difficulty of stopping the process of· solution at a precisely significant point, but it is interesting to note that A. Fry found that nitrided iron (i.e. 'ammonified' iron) retained 0.5% nitrogen after being heated to redness. This figure thus represents a significant stage in the retention of nitrogen by iron however it may have been introduced.

Weight Changes when Iron of High Purity is heated in Pure Nitrogen

In connection with our previously published results it was felt to be desirable to investigate the matter of weight loss in order to see whether the losses in weight which occur when iron and its alloys are heated in nitrogen could be correlated with the various factors concerned. It was satisfactorily proved that the carbon was attacked by the nitrogen and it now remained to be proved whether the iron itself took part in the formation of a volatile compound. The results obtained were not very conclusive owing to the innate experimental difficulties attaching to the problem. It may be, however, that a brief résumé of our results might be of value to some future workers in this field.

In the first place the method adopted by previous workers was tried, namely, that of heating small weighed quantities in a boat. This method showed considerable discrepancies which were traced to the alterations in the weight of the boats themselves. None of the materials used were found to be capable of being heated in a stream of nitrogen when carrying a load of iron without undergoing serious changes in weight. Silica boats decrepitated and were subject to moisture changes; fireclay boats were found to absorb both moisture and oxygen during weighing and handling operations; iron boats changed weight during the heating operation. A long series of experiments may be summed up by saying that the most consistent results were obtained

by using iron boats which had been 'stabilized' to the experimental conditions by having been heated in nitrogen until there occurred no further change in weight. Such boats were covered with the transparent layer and did not show the weight changes during handling usually associated with the absorption of moisture or air.

Stabilisation of N. B. 4 and N. B. 5.

N. B. 4, when heated to 1000°C three times for 5 hour periods first lost 0.063% of its weight, then lost a further 0.003% and after a third heating became constant in weight.

N. B. 5 also became constant in weight after being heated in nitrogen three times to 1000°C.

Weight Changes when Iron Powder is heated in Nitrogen in a 'Stabilised' Iron Boat

Form of Iron	Temperature of Nitrogenation	Change in Weight (Grammes and Percentage)
Powder dehydrogenated at 600°C	1000°C	−0.0032 gms. or −0.28%
Dehydrogenated powder once nitrogenated	1000°C	±0.0000 gms. or ±0.0%
Re-ground twice nitrogenated powder	1000°C	−0.0004 gms. or −0.04%
Powder dehydrogenated at 600°C	1000°C	−0.0065 gms. or −0.4%
Previously nitrogenated	1100°C	−0.0020 gms. or −0.14%
Powder dehydrogenated at 600°C	1000°C	−0.0052 gms. or −0.28%

The above results show that powdered iron prepared by the method described above, when heated in nitrogen at 1000-1100°C, loses 0.3−0.4% of its weight and then becomes constant in weight.

Accordingly, results obtained by previous workers and which shew an absence of positive weight changes when ferrous materials are heated in molecular nitrogen are not very good evidence of the inertness of molecular

nitrogen towards iron. Further, seeing that ferrous alloys lose carbon when heated in nitrogen, that other constituents of the alloys may be affected and that the material of the containing boat is so easily affected by the experimental conditions it is clear that weight changes in ferrous alloys require very careful interpretation before inferences of value can be deduced therefrom. That is the chief value of the above results. A more consistent set of weight changes are available, carried out as they were on 'massive' specimens of Crookes electrode, without the intervention of a boat. These figures show a slight gain up to 700°C, after which there is a loss and again at the highest temperatures there is no appreciable change of weight. Taken in conjunction with our weight changes obtained with iron-carbon alloys these three sets of change may be interpreted as showing

(a)   the film formation especially noted about 500°C, this film being ordinary iron nitride;

(b)   Removal of the small amount of carbon shown in the analysis in the range 700–800°C;

(c)   Substitution of nitrogen for the replaced carbon in the third range up to 1100°C.

Weight Changes in Crookes Electrode when heated in Nitrogen (without a boat)

Form of Iron	Temperature	Initial Weight gms.	Final Weight gms.	Change in Weight gms.
Crookes Electrode	500°C	2.0056	2.0057	+0.0001
Crookes Electrode	700°C	2.3542	2.3539	−0.0003
Crookes Electrode	750°C	3.2600	3.2590	−0.0010
Crookes Electrode	1100°C	4.7051	4.7051	±0.0000

In connection with the above table it will be of interest to point out that the Crookes electrode when heated in a vacuum underwent no change in weight and when heated in ammonia gas it gained 0.67% at 750°C and 0.2% at 1100°C. (No glassy layer formed.)

Solution Tests

The original and most important test of the action of molecular nitrogen on iron is the resultant loss of solubility in hydrochloric acid.[1] Normally iron is easily dissolved by hydrochloric acid; this was constantly confirmed during our experiments. Not only is the evidence of decreased solubility here put forward as the most convincing proof that nitrogen does act on iron but the following tests were done to show that the 'resistivity' towards hydrochloric acid is mainly a matter of the action of nitrogen on iron. This latter point could not be considered proved until the action had been narrowed down to nitrogen and pure iron such as was prepared for use in these experiments.

[1] Gray: loc. cit.

Resistance to N/2 Hydrochloric Acid of Nitrogenated Electrolytic Iron

Form of Iron	Behaviour
Untreated flakes of electrolytic iron.	Gassed immediately. Dissolved rapidly whilst being watched; left no residue.
Electrolytic flakes nitrogenated at 700°C.	After 5 hours in acid were found to be gassing slowly: after 24 hours the flakes had dissolved except for a thin film which, after 48 hours, was found to be broken down to a fine powder. The powder did not show signs of dissolving further.
Electrolytic flakes nitrogenated at 1100°C.	After 8 days in acid no solution had occurred and potassium thiocyanate gave a negative test for iron when applied to the acid in which the flakes were immersed. The flakes were slightly dulled in appearance but no gas was being evolved. After 15 days there were slight signs of attack shown by a very slow evolution of gas. After 24 days a film was seen to be separating which, after 5 months' immersion in the acid retained its shape and did not break down on shaking the containing flask. A portion of this film was taken out and photographed at the end of 60 days.

This resistance to dilute hydrochloric acid of the nitrogenated flakes which were calculated to be of the order of 0.0003 cm. thick establishes quite definitely that the resistance is a matter in which the nitrogen and the iron alone are concerned. That oxygen and the possible oxide film are concerned is not likely in view of our experimental precautions and in view of the experience of U. R. Evans, who informs me privately that in his early experiments he found that oxide films on ferrous materials dissolved very rapidly in dilute hydrochloric acid when in contact with the underlying metal (as our films always were). Mr. Evans very kindly allows me to quote him to the effect that "I do not think that any ferric oxide film which is likely to be produced on ordinary iron or carbon steel (free from such special elements as nickel or molybdenum) would survive long in contact with the metal if the metal carrying it is placed in dilute hydrochloric acid, since the oxide will usually suffer reduction to ferrous oxide which will quickly dissolve; the stripped films, if once out of contact with the metal are more resistant towards acids."

The above results may be taken as establishing the effect which nitrogenation has on electrolytic iron but they are necessarily observational in character. The fragmentary nature of the films rendered handling for weighing purposes inadvisable. The quantitative effect has already been demonstrated in previous papers and these results were designed to show that it was the iron which, in ferrous alloys, is chiefly affected.

Using Crookes electrode as a sample of iron of a high degree of purity but available in a weighable form it may be mentioned that after 24 hours'

immersion in N/2 hydrochloric acid the polished un-nitrogenated electrode lost 0.4% of its weight whereas the nitrogenated polished electrode lost 0.08% of its weight.

Similarly a sample of sheet iron of high commercial purity lost 6.02% of its weight after 24 hours' immersion in the dilute hydrochloric acid whereas a piece of the same material, after being nitrogenated for 16 hours at 1000°C, lost only 0.43% of its weight under the same circumstances.

In all these three cases it is the reaction between the iron and the nitrogen which is the cause of the resistivity towards hydrochloric acid. 'Impurities' such as are invariably present in ferrous alloys will modify the effect of the nitrogenation on the solubility of the material because they modify greatly the amount of iron available for the action of the nitrogen. The effect of one impurity, namely, carbon, has been found to be adverse but it may be that further experimentation would show that some impurities can be so acted on by nitrogen that the resistivity can be increased. The question of the depth to which resistance to attack by hydrochloric acid can be effected by nitrogen is of importance since any penetration beyond the surface means that no mere surface effect is concerned. Similarly the effect cannot be dissociated from the nitrogen atmosphere by suggesting thermal or annealing effects as the cause of the resistivity to hydrochloric acid. If this were the case it would be difficult to see why the resistance to acid should not penetrate throughout the whole of any nitrogenated specimen. Our experiments show that whilst the transparent crystalline layer is the most obvious and serious bar to solubility in hydrochloric acid the resistance to the acid does persist even when the layer has been removed and it can be traced to a measurable depth in the ferrous material. In other words the rate of solution of the nitrogenated material is greater the further away it is from the surface. This was demonstrated by our being able to eat away with hydrochloric acid the centre portion from a fractured nitrogenated pencil whilst the surface remained resistant to the acid. This one experiment showed that the physical explanations of the resistance to acid are not satisfactory whether one adopts the surface change or the allotropic annealing variety of explanation. The facts of the situation demand an explanation which accounts for a measurable penetration to a greater or less depth depending on the extent to which the nitrogen has been able to react with the iron. The chemical action of nitrogen supplies such an explanation. This action results in the formation of a transparent crystalline layer which is thicker and more obvious at 1100°C than at 700°C. This layer then interferes with the action of gaseous nitrogen but reacts with the underlying iron to render it resistant to the action of hydrochloric acid. Before leaving the subject of solubility there may be put on record the effect of ammonia gas on the solubility of Crookes electrode. e. g.

Loss after 24 hours in N/2 hydrochloric acid:—

(a) untreated electrode lost   0.4% in weight
(b) heated in ammonia gas at 1100°C lost   6.5% in weight
(c) heated in ammonia gas at 750°C lost   10.4% in weight

When these figures are compared with the effect of nitrogenation it is seen that whereas nitrogenation effected a reduction in solubility of 80%, 'ammonification' increased the solubility to a figure ranging from 16 to 24 times that of the original and untreated electrode.

This affords an interesting and convincing proof of the difference between the action of ammonia and that of nitrogen on iron.

Isolation of the Insoluble Layer

The hesitation which was at first felt about ascribing the resistance of nitrogenated iron towards hydrochloric acid to the formation of an insoluble
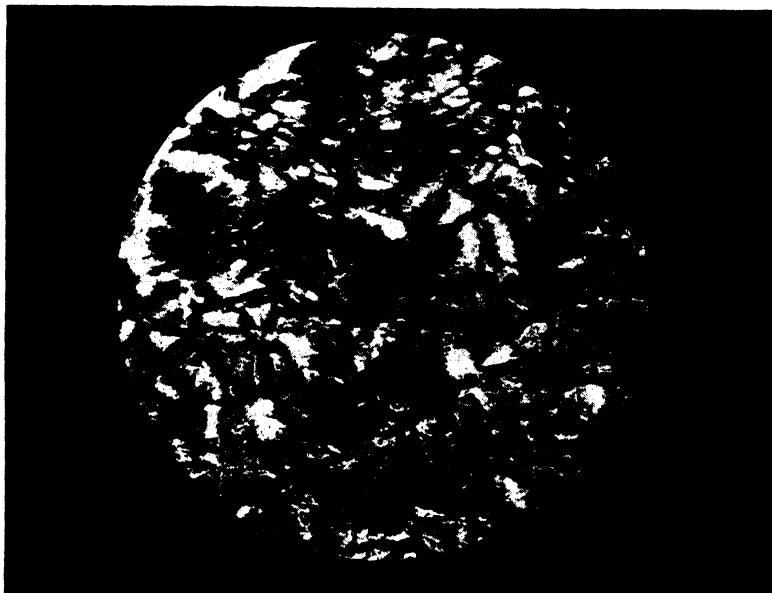
FIG. 3

Insoluble layer left after electrolytic iron flake nitrogenated at 1100°C had been allowed to stand in N/2 hydrochloric acid for 2 months. Transmitted light × 412.

layer disappeared when the layer was found capable of isolation. The first occasion on which this occurred was when a portion of nitrogenated iron wire was left indefinitely in dilute hydrochloric acid to see how it would be attacked. The iron core disappeared, leaving a tubular shell of yellowish white material; this shell, although it appeared to be capable of turning brown on long exposure to the atmosphere and so suffering oxidation, did in fact behave as if it were insoluble in hydrochloric acid.

Accordingly a sample of electrolytic iron, nitrogenated at 1100°C was left in N/2 hydrochloric acid for 2 months. At the end of this time the insoluble film, from which the free iron had been practically entirely extracted, was transferred to a microscope slide and photographed by transmitted light. The heavily etched film (see Fig. 3) which, by its behaviour to hydrochloric acid, is evidently neither iron nor iron oxide, shows signs of differential dis-

solution which strongly suggest a duplex structure in the original layer from which it has survived. The nature of this duplex layer has not been established. In this connection it will be recalled that the electrolytic flake from which the isolated layer was obtained was purposely prepared very thin in order to allow the nitrogen to attack the iron from both sides so as to obtain a thorough nitrogenation. That being so, any tendency to settle down, under equilibrium conditions into a duplex structure, would be more marked in the case of the electrolytic flake than it would in the Crookes electrode. As noted above, the microscopic observations confirmed this view.

The Double Polygonal Grain System

The above record of experimental observations has established in the minds of the authors the following main points:—

(1)   Nitrogen and iron react.

(2)   The reaction product, about which it would be unwise to dogmatise from the point of view of composition, is difficult to dissolve in dilute hydrochloric acid.

(3)   The surface of the nitrogenated iron is covered with a transparent glassy film which reveals a double polygonal grain structure. This transparent film makes its appearance at and above 700°C.

(4)   Experiments on iron-carbon alloys show that the film is not formed until the carbon has been removed by the nitrogen. This suggested (and the suggestion was verified by the above experiments) that the formation of the insoluble layer is due to the nitrogen and iron alone.

(5)   The penetration of the insolubility to the interior of the nitrogenated iron for a definite depth but not necessarily through the whole mass of the material makes it clear that we are not here dealing with either a surface change or a homogeneous allotropic change brought about by temperature alone. That is to say that it is a change brought about by the presence of the nitrogen. Molecular nitrogen is not inert to iron and to heat iron in nitrogen is not the same thing as heating it in a vacuum. At temperatures in the neighbourhood of 500°C we have little doubt that the reaction product might prove to be iron nitride itself in the form of the grey film. At 700°C and above the appearance of fusion and the transparent layer suggest that questions of duplex structure, involving the formation of eutectic materials together with the possibility of solid solution format'on, will arise in any further work which may be done on this subject. In fact there seems to be no valid reason to suppose that the product of the action of nitrogen on alpha iron is necessarily the same as the product of the action of nitrogen on gamma iron.

During the course of preparing this paper for publication, the attention of one of us was kindly drawn by Professor Desch to the work of Rosenhain and Humfrey[1] and that of Kroll[2] with a view to showing that double polygonal grain structures can be obtained without the intervention of nitrogen. The

[1] Proc. Roy. Soc., **83**, 200-209.

[2] J. Iron Steel Inst., 1910, 304.

photographs published by these workers are of the highest significance in connection with our work but in no way conflict either with our results or our conclusions. The samples used by Rosenhain and Humfrey were previously heated and cooled in hydrogen gas, a procedure which was shown by Kroll to produce the double polygonal grain structure which we also get with nitrogen. Occasionally, but by no means always, the hydrogenated samples were then heated in vacuo. It was after this treatment that Rosenhain heated the polished specimen and obtained the double structure. Now our experiments clearly show that merely heating in vacuo produces a faint grain structure due to de-gassing. This structure is, however, quite faint and markedly dissimilar to the nitrogenation structure produced at the same temperature. Furthermore Rosenhain interpreted the structures he obtained in the light of the alpha, beta and gamma forms of iron which at that time were supposed to form separate phases during the heat transformations of iron. In the published photograph referred to Rosenhain specifically mentions the oxide coating which overlay the other structure. This oxide coating in no way interfered with his experimental results and inferences but every volume of oxygen was necessarily accompanied by four volumes of nitrogen. Accordingly it seems to us that the classical experiments of Rosenhain and Humfrey have no direct bearing on our work especially from the point of view of the solubility in dilute hydrochloric acid which we are inclined to stress both on account of its novelty and its possible future theoretical significance.

The work of Kroll, in which he shows a very well developed case of double (at least) polygonal grain structure, was also intended to support the alpha, beta, gamma theory of the allotropy of iron. The samples of iron were heated in hydrogen to 950°C. At the time that these experiments were performed this temperature of reaction would of necessity raise the question of the three allotropic forms of iron. Our experiments on the other hand involve no such considerations since at 700°C the heating in nitrogen produces definite signs of the transparent layer; these are reinforced at 750°C without in either case the iron having entered the temperature zone which produces the gamma form of iron. Neither at 700 nor at 750°C is the transparent layer formed in the absence of nitrogen.

It is, in the opinion of the present writers, of the highest significance that Herr Kroll should point out that at this temperature Roberts Austen noted that hydrogen alters the transformation point of iron and further that Heyn detected at this temperature considerable absorption of hydrogen. There is, as yet, no agreement as to the precise difference between adsorption and chemical combination and research workers seem to use the two terms more as a matter of convenience than as a matter of proved conviction. It is at this point however that the work of Kroll begins to be of direct significance to our results. Just as the solubility of hydrogen in iron reaches significant dimensions at or about the reaction temperature used by Kroll so does Jurisch[1] note that the solubility of nitrogen increases to a marked extent in

[1] J. Chem. Soc., 1915 A II, 56.

iron at or about 930°C. It is not the province of this paper nor have we the necessary data to discuss the relationship between adsorption, solubility, solid solution and compound formation. It does seem, however, as if the quoted observations as to the solubility of hydrogen and nitrogen taken into consideration alongside the accepted view of the double solid solution formation in the case of hydrogen and palladium would lead to an explanation of the occurrence of the double polygonal grain structure. In both the case of hydrogen and nitrogen there is at least a possibility of the formation of a compound with the iron. The solubility is a certainty. The nature of the hydrogen-palladium equilibrium curve is most readily explained on the supposition that there are two solid solutions in that case. This supposition will have its structural counterpart. Consequently it is here put forward as a tentative suggestion that the multiple structures obtained in our experiments are connected with the specific action of nitrogen on iron but that, just as in the case of hydrogen and palladium, there may be more than one phase concerned. For the present it is not considered advisable to dogmatise as to the precise nature or composition of these. We do consider, however, that we have evidence that the transparent crystalline layer, whatever its ultimate stoichiometric composition may prove to be, will be found to possess a duplex or eutectic structure, when nitrogenation experiments are done under equilibrium conditions. The above experiments, being chiefly concerned with the establishment of the phenomenon, are not considered by us to have been done under such conditions.

Summary

Experimental proof is adduced that molecular nitrogen acts on alpha and on gamma iron.

The most important evidence consists in the relative insolubility of the nitrogenated iron.

Other evidence is to be found in the microscopic examination and in the nitrogen absorption.

The insoluble layer has been isolated, examined and photographed by transmitted light.

DISCONTINUITY OF THE ISOTHERMALS FOR THE ADSORPTION OF PHENOL FROM SOLUTION

BY R. CHAPLIN

In the course of an investigation on an industrial use of active charcoal, which need not be described here, it became necessary to determine at 25° and 60° the adsorption isothermals for a technical active charcoal and phenol in aqueous solution at concentrations lying between 0.1 and 24.0 grams/litre. The results obtained were unusual in that they showed pronounced discontinuity in the relation between quantity of phenol adsorbed and concentration of the solution. In view of suggestions of discontinuity in adsorption processes which have appeared in the literature from time to time,[1] and particularly in view of a recent paper on the subject by Allmand and Burrage,[2] it was felt that these results might be of academic interest.

The charcoal used in the investigation referred to was of the extruded type, activated by the zinc chloride process and had no exceptional properties in any way. The discontinuity observed, therefore, would seem at first sight to be characteristic of the sorbate. But it may be that phenols merely show up in a pronounced way a phenomenon which is characteristic of the adsorption process in general, and this is the real point of interest. Data for other sorbates, obtained under the conditions described below, would be helpful in further elucidating the matter.

A working description of the method used, and the results obtained, are given in what follows.

Experimental Method

The apparatus used consisted simply of a 300 c.c. wide-necked flask fitted with a bung carrying a small glass stirrer and a short, corked tube 1 cm. in diameter, which served for the withdrawal of solution or the introduction of water.

220 c.c. of water at 25°C. or at 60°C. were run into the flask, the requisite weight of pure phenol added and the flask was corked and immersed to the neck in a bath at 25°C. or at 60°C. Stirring was commenced and after the adjustment of temperature 20 c.c. of solution were withdrawn for analysis. The phenol was estimated in the usual way by Koppeschaar's bromination method[3] which was found to give results accurate to within 1% of the phenol present. The bung was then removed and about 2 grams of charcoal, previously dried at 130°C. in a U-tube and weighed therein, were introduced. The bung was quickly replaced and the charcoal and solution were stirred together for 3 hours, after which samples of solution were withdrawn for

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[1] Recently N. Semenov: Z. physik. Chem., 1930 B7, 471.

[2] Proc. Roy. Soc., 130 A, 610 (1931).

[3] Z. anal. Chem., 15, 233 (1876).

analysis.   The quantity of phenol adsorbed was calculated from the fall in concentration and the total bulk of solution, and was then referred to unit weight of charcoal and plotted against the final phenol concentration.

For the approximate isothermal given in Table I successive points were obtained by increasing the phenol concentration above that for the preceding point, following the procedure just described, and adding the value for phenol adsorbed to that previously calculated, the total phenol adsorbed at any stage being plotted against the corresponding final concentration. Such a method evidently gives rise to cumulative error and this was found to be very considerable in the present case after the determination of a number of points.   The error is mainly due to the slowness with which equilibrium is finally approached in the adsorption of phenol from solution and, in order to avoid it, fresh charcoal was used for each point of the isothermals given in Tables II and III.   The use of fresh charcoal for each point conduces to much greater accuracy in work of this kind and tends to reveal the true form of isothermal.   The only exceptions to the new procedure are the few desorption points shown by the letter D in Table II (crosses in Fig. 2) which were unavoidably dependent on a prior sorption point.   For the determination of these the solution in contact with the charcoal at the conclusion of sorption was diluted with water and the quantity of phenol withdrawn was calculated from the rise in phenol concentration above that corresponding to dilution.

The time of contact adopted was decided on as a result of rough velocity measurements (not given) at 25° and 60°.   These showed that after 3 hours the adsorption became comparatively slow and the results could then be sufficiently well reproduced.

Results

TABLE I

60° Phenol Isothermal (approximate values)
A = Phenol Conc., grams/litre
B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.6	140	15.5	365
1.2	165	16.0	410
2.0	185	18.6	410
9.2	200	21.0	410
11.0	200	24.0	453
16.0	215		

The results in Table I are plotted in Fig. 1 (isothermal 1).
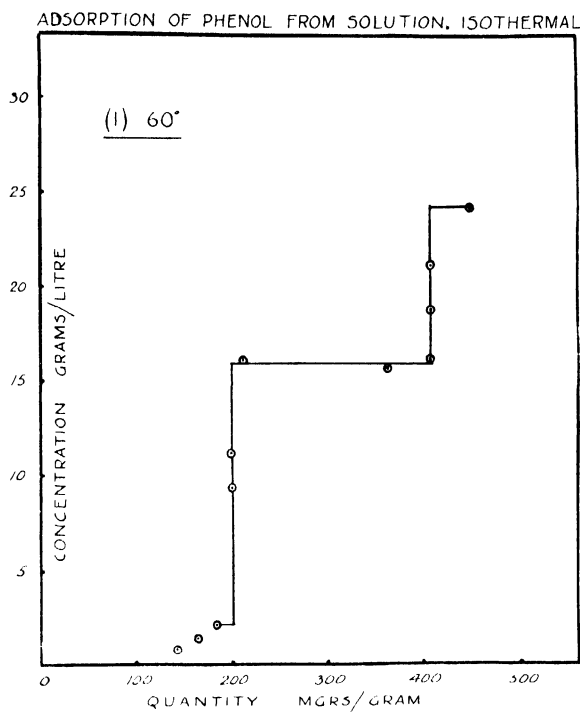
FIG. 1

TABLE II

60°C. Phenol Isothermal

A = Phenol Conc., grams/litre

B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.14	52	D 0.64	138
0.22	81	2.06	186
0.33	98	D 1.20	166
0.40	128	3.07	192
D 0.28	128	D 2.39	188
1.04	152		

TABLE III

25°C. Phenol Isothermal

A = Phenol Conc., grams/litre

B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.10	65.5	0.96	151.0
0.24	93.5	1.43	167.5
0.37	120.0	1.45	191.5
0.49	123.0	1.81	187.0
0.68	124.0	2.24	190.0
0.70	136.0	3.00	191.0
0.78	136.0		

ADSORPTION   OF   PHENOL   FROM   SOLUTION.   ISOTHERMALS.
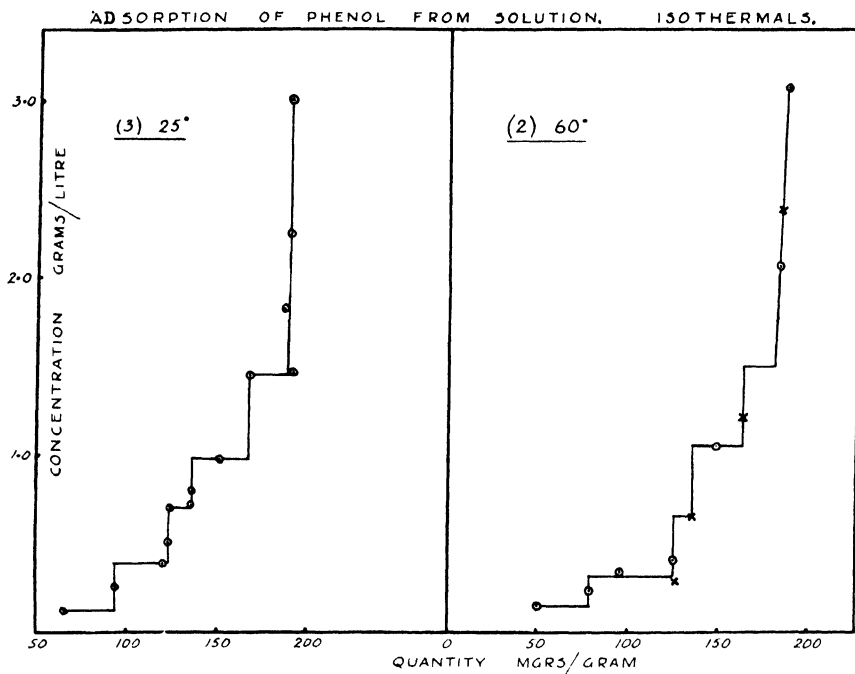
Fig. 2

The results in Tables II and III are plotted in Fig. 2 (isothermals 2 and 3).

Discussion

Isothermal 1 extends up to concentrations some 10 times as high as those of isothermals 2 and 3 but it gives no information as to form at low concentrations. Accordingly in the determination of isothermals 2 and 3 the concentrations have mainly been kept below the value at which isothermal 1 begins and these isothermals have been plotted on a more open scale.

There is perhaps some choice as to how the points may be joined up—particularly the lower terminal points—but taking the three sets of results into consideration the discontinuous nature of the isothermals can hardly be doubted. The most convincing case is isothermal 3 in which several of the experimental points were determined as nearly as possible at the turning point values. The exact form of the isothermals could, of course, only be determined by taking a considerably larger number of points than was here done.

The large increase in phenol content of the charcoal without further increase in concentration of solution which occurs at 16 grams/litre, shown in isothermal 1, recalls the behaviour of charcoal with water vapour at 12–15 m.m. partial pressure.[4]

The author's thanks are due to the Gas Light & Coke Company, in whose Fulham laboratories the work was done, for permission to publish these results.

November 10, 1931.

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[4] Allmand, Chaplin and Shiels: J. Phys. Chem., **33**, 1151; Allmand and Hand: 1161 (1929).

AN EXPERIMENTAL INVESTIGATION OF THE PHASE RELATIONS OF K₂Si₄O₉ UNDER PRESSURE

BY ROY W. GORANSON AND F. C. KRACEK

Introduction

In order to solve many of the problems of geophysical chemistry, in particular of the silicates, the effect of pressure on phase equilibria must be evaluated. Such investigations on silicate systems require the simultaneous use of high temperatures and pressures. To this end apparatus has been designed and some progress already made.

Many silicates are extremely sluggish in crystallizing and, furthermore, in many instances crystalline silicates can be superheated several degrees above the melting temperature. Hence no one method of attack or technique is applicable for all.

In this paper are presented experimental results of the effect of pressure on the phase relations of a unique compound, potassium tetrasilicate($K_2Si_4O_9$).

Description of Potassium Tetrasilicate

Although this compound is unimportant geologically because it has a rather limited field of stability at the liquidus,[1] forms a hydrate at lower temperatures, and is attacked by CO_2 in moist air, its abnormal behavior makes it unique among the silicates.

At one atmosphere pressure the compound melts at $765°C$, which is one of the lowest melting points encountered among the silicates. In the binary system, K_2O-SiO_2, the liquidus curve of the compound extends from 69 to 72 weight per cent SiO_2, the neighboring crystal phases being $K_2Si_2O_5$ and quartz, with which it forms eutectics at $752°$ and $764°$, respectively.

Glass of composition $K_2Si_4O_9$ is so inert that many days' treatment at temperatures only 10–15° below the melting point of the compound fails to produce appreciable amounts of crystals, and even when seeding is resorted to, the growth of further crystals takes place very slowly. The compound can, however, be crystallized with moderate rapidity when water is used as a "catalyst."[1] It is essential, however, to use not more than the necessary minimum amount of water since otherwise a hydrated phase, $K_2Si_4O_9.H_2O$, is formed[2] which on dehydration generally reverts to glass, or to a mixture of crystals and glass.

The optical data of $K_2Si_4O_9$ are as follows:[1] refractive index of glass, 1.495; of crystals, $\alpha = 1.477$, $\gamma = 1.482$, with $2V$ possibly large.

[1] Kracek, Bowen, and Morey: J. Phys. Chem., **34**, 1857 (1930).
[2] Morey and Fenner: J. Am. Chem. Soc., **39**, 1173 (1917).

The densities were determined by suspending the material in mixtures of bromoform and carbon tetrachloride and a Westphal balance used for measuring the density of the liquid in which the grains remained suspended. The crystalline grains invariably formed a close-knit porous structure of fine grains, hence, although due care was taken to expel the air from the grains by evacuation before and after immersion in the liquid, the measured density may be incorrect in the third decimal place. This source of error was not present in the case of the glass. Density of $K_2Si_4O_9$ glass at 20°C, 2.384; density of crystalline $K_2Si_4O_9$ at 20°C, 2.335.

Pressure Investigation

Description of Bomb

The bomb[1] consists essentially of a chrome vanadium steel cylindrical shell capped at each end by steel lids. These lids are sealed to the cylindrical shell by means of copper gaskets, the whole being held together by means of a 500 ton oil press. Thermocouple wires for reading temperatures pass into the bomb through special electrically insulating leak-proof packings in the upper lid. Leads for the furnace pass into the bomb through similar packings in the lower lid. The furnace is made by winding platinum-rhodium wire on a "Sillimanite" tube. Care is taken to obtain as much thermal insulation as possible between the bomb walls and the furnace. The bomb walls are further protected from over-heating by means of circulating water.

For the melting experiments at pressures above 900 bars (metric atmospheres) carbon dioxide was used as the pressure medium; for the lower pressure melting experiments and in the inversion experiments nitrogen was used. Pressure was obtained in two stages: initially, as much as 1800 atmospheres can be obtained by compressing the gas in a Watson-Stillman intensifier with a hand pump; secondly, the gas becomes heated as the temperature of the furnace rises and, since the volume remains constant, the pressure must increase. This increase in pressure is considerable in the case of carbon dioxide which is injected into the bomb as a liquid.

Pressure was read on Bourdon-type gauges calibrated against an Amagat-type dead-weight gauge. Pressures from 1 to 500 bars[2] were read with an accuracy of ± 0.5 bar; for pressures above 500 bars the error of reading was ± 10 bars.

Temperature was read by means of platinum-platinum rhodium thermocouples. In the early stages of the work connection of these leads through the bomb lid was made by using compensating leads of nichrome and iron through the packings. These leads caused considerable temperature fluctuation due to inequalities of temperature distribution at the junctions. They were later discarded and the platinum and platinum rhodium leads carried directly through the packings into the bomb, thereby eliminating all such fluctuations. The earlier experiments are estimated as good to ± 3°; in the later experiments the temperature could be controlled and read to 0.1°C.

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[1] For a more detailed description and diagram of the bomb see Roy W. Goranson: Am. J. Sci., **22**, 481 (1931).

[2] 1 bar = 10⁶ dynes per cm.²

Experimental Detail

Pressure melting curve. A simple modification of the quenching method was used in determining the melting curve. This was made possible by the fact that the vitreous phase of potassium tetrasilicate does not crystallize readily near its liquidus temperature.

Charges of crystalline potassium tetrasilicate were inserted in gold capsules made from gold tubing. After the powder had been inserted the upper end of the capsule was pinched together and sealed in an oxy-gas flame, keeping the lower end of the capsule in water to prevent possible fusion of the tetrasilicate.

Two such capsules were used in each run as occasionally a capsule was found to be defective. A defective capsule would allow CO_2 to enter and react with the tetrasilicate. The capsules were tied to the temperature-reading thermocouples but were electrically insulated from them. The thermocouple column and charges were then inserted in a silica glass test tube which fitted closely into the furnace. The intervening space in the tube was filled with silica glass sand in order to lessen temperature fluctuations from gas convection.

The duration of a run was from one-half to one hour after reaching the desired temperature and pressure. It was found that a fifteen-minute interval at the liquidus was sufficient time to melt the crystals.

Pressure-inversion curve. In these experiments the temperature was also read by means of a Pt-Pt Rh thermocouple. The differential temperature, *i.e.*, the difference

FIG. 1

Sketch of crucible assemblage for obtaining the pressure-transition curve of $K_2Si_4O_9$

in temperature between the inert body, in this case silica glass, and potassium tetrasilicate was obtained by using platinum against gold-palladium (40% Pd). The crucible and the arrangement of the thermocouples is shown in Fig. 1. The thermocouple wires were sealed to the leads passing through the lid of the bomb. A silica glass test tube was slipped over this assembly and the remaining space in the tube filled with silica glass sand as in the melting experiments. In the inversion experiments the tetrasilicate was exposed to the gas in the bomb. Since carbon dioxide was found to react with the crystals, nitrogen was used as the pressure medium.

Experimental Results

Pressure-melting curve. The experimental results are tabulated in Table I. The temperatures listed in the table are temperatures as given by L. H. Adams (International Critical Tables, vol. I, p. 57) plus a correction of 3°C for the

thermocouples used. The pressures listed have been corrected from a deviation curve prepared by calibrating the gauges used against an Amagat-type dead-weight gauge.

TABLE I

Pressure melting of $K_2Si_4O_9$

Corrected pressure in bars	Corrected temperature in °C	State
1	765	melting point (Kracek, Morey, and Bowen)
1	765	glass
1	763	crystals
102	750	crystals
287	745	glass
290	740	crystals
470	726	crystals (some glass present)
500	730	glass with rare crystals
930	894	glass
930	772	glass
930	743	glass
930	716	glass (may be a few traces of crystals left)
930	681	crystals
930	697	crystals
930	710	crystals
1290	702	glass
1300	693	crystals
1310	697	glass
1300	695	glass
1490	681	crystals
1610	685	glass
1680	678	crystals
1770	681	glass
1855	669	crystals (a small amount of glass)
1870	672	glass
2050	664	glass
2140	659	crystals
2600	637	crystals
2710	637	rare crystals (some melting has occurred)

Pressure-inversion curve. Potassium tetrasilicate crystals pass through an inversion at a temperature only a few degrees above the inversion in quartz ($573°$). This transition is remarkably prompt, but apparently not definitely isothermal. The existence of this inversion was inferred from a study of the pressure-volume relations on melting.

Typical differential heating and cooling curves of the transition at atmospheric pressure are reproduced in Fig. 2, and at 103 and 420 bars pressure in Fig. 3. The character of the curves indicates that the transition may be
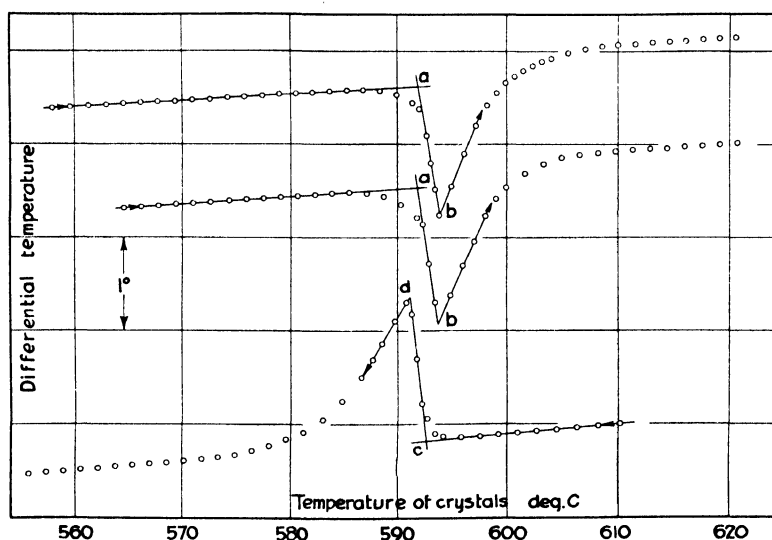
FIG. 2

Heating and cooling curves through the inversion of $K_2Si_4O_9$ at atmospheric pressure
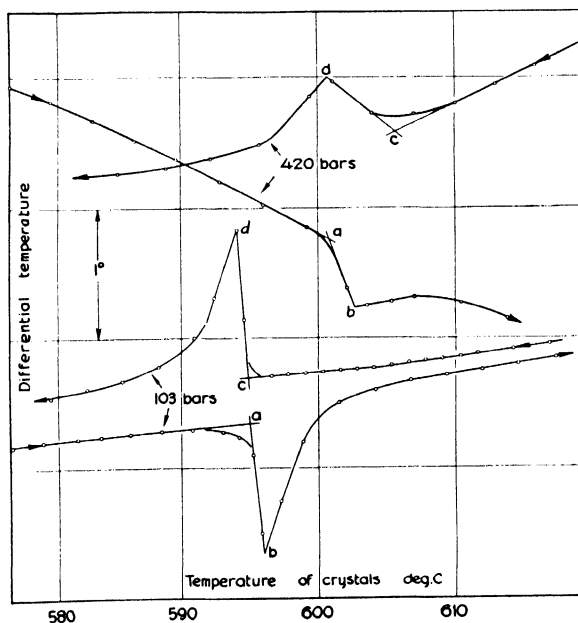
FIG. 3

Heating and cooling curves through the inversion of
$K_2Si_4O_9$ at 103 and 420 bars pressure

initiated gradually so that its actual beginning can not be located accurately. We have therefore adopted the convention of producing the straight lines typical of the transition loop (see Figs. 2, 3) to meet at points a, b, c, d, and calling the points a and c the beginning of the transition on heating and cooling respectively. It is of interest to note that the transition has very little hysteresis, since point c is either at the same or a higher temperature than point a. At atmospheric pressure the point a is at 592°, point c at 593°.

The results are tabulated in Table II. In column 2 are given the temperatures of the beginning of the inversion on heating (point a), and in column 3 the beginning of the inversion on cooling (point c).

<div align="center">

TABLE II

Pressure inversion of $K_2Si_4O_9$

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Pressure in bars	Temperature in °C	
	Beg. of inversion on heating (point "a")	Beg. of inversion on cooling (point "c")
1	592	593
1	592	594
1	589	594
57	595.0	595.0
103	595.3	595.4
104	589.0	593.2
144	593.0	595.4
145	593.2	—
204	597.0	600.2
420	599	603.4
419	600.0	—
940	617.7	615.2
940	615.0	615.0

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Temperature-pressure Phase Relations of $K_2Si_4O_9$

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The experimentally determined temperature-pressure phase diagram for $K_2Si_4O_9$ is given in Fig. 4. Along the melting curve open circles denote the liquid phase and black circles the crystalline phase. Along the inversion curve circles dark in the upper half segment denote inversion temperatures on heating, those dark in the lower half segment denote inversion temperatures on cooling, and black circles indicate that the inversion temperatures for heating and cooling coincided.

The triple point for the two crystalline forms of $K_2Si_4O_9$ and liquid is estimated to be at 654°C, 2275 bars.

The larger portion of the field labelled "Liquid" is metastable, and it was not possible to obtain the stable phases experimentally with the apparatus as arranged at that time. Both quartz and potassium disilicate crystallize very slowly at these temperatures and therefore the time interval would have had to be increased beyond that available.
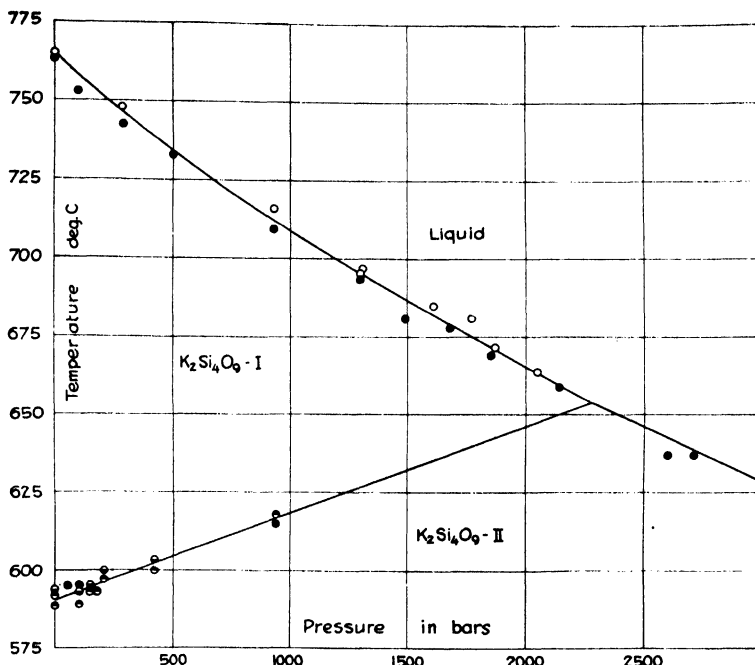
FIG. 4

Experimental temperature-pressure phase diagram of $K_2Si_4O_9$. The solid-liquid boundary above 140 bars is metastable

In order to obtain the phases and fields of stable equilibrium it is necessary to consider the portion of the system, K_2O-SiO_2, adjoining potassium tetrasilicate. This is discussed later under "Stability of $K_2Si_4O_9$."

Calorimetric Investigation

Experimental Procedure

The heat of melting and heat of inversion of $K_2Si_4O_9$ at atmospheric pressure were measured by the differential heating curve method, following strictly the procedure described in an earlier paper.[1] The apparatus employed was the same as in the earlier work, with minor structural modifications. Au Pd-Pt Rh thermocouples (40% Pd, 10% Rh) were used for measuring the temperature and the differential temperature. These were checked at a number of standard points, and appropriate corrections were applied, using the comparison table by L. H. Adams (International Critical Tables, vol. I, p. 59).

The choice of the heating curve method of latent heat measurement was made as a compromise. Since $K_2Si_4O_9$ glass does not crystallize rapidly, the method of mixtures is not applicable, and accordingly, the only alternative

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[1] F. C. Kracek: J. Phys. Chem., **34**, 225 (1930). A modification of the heating curve method developed by Thomas and Parks: J. Phys. Chem., **35**, 2091 (1931) appeared after our work was completed.

was the method of solution of the glass and of the crystals in hydrofluoric acid separately, in conjunction with the determination of the heat capacity of the glass and of the crystals between the melting point and the temperature of the solution calorimeter. The cumulative errors to be expected from this procedure are so large that the method was kept in view only as a possibility for use if the heating curve method failed to yield usable results.

Experimental Results

The time-differential temperature areas for the calibration of the thermal equivalent of the apparatus in calories per 1000 microvolt minutes are given in Table III. A straight line through the points plotted against the temperature yields, in whole calories, 24 cal. per 1000 μvm at 765° and 19 cal. per 1000 μvm at 592°, the melting and inversion points, respectively, of $K_2Si_4O_9$ at atmospheric pressure.

TABLE III

Calibration of Apparatus for Latent Heats

Calibrating substance	t°C	Latent heat cal/g	Equivalent area cal/1000 μvm	Number of determinations
KCl[1] melting	766	86	24.5 ±10%	4
K_2CrO_4[2] inversion	665	12.6	21.5 ±10%	3
K_2SO_4[2] inversion	588	13	19.2 ±10%	4
$PbCl_2$[3] melting	490	20	14.8 ±10%	4

Heat of melting. A typical heat of melting area for $K_2Si_4O_9$ is reproduced in Fig. 5. Three experiments gave 33, 34, and 36 cal. per gram for the heat of melting. We adopt as average the value 35 cal. per gram (146.5 joules per gram).

This value of 35 cal. per gram is estimated to be in error by ± 20%, in spite of the rather close agreement between the individual experiments, for the reason that the melting of $K_2Si_4O_9$, like that of most silicates, is not an isothermal process. In addition to the errors due to this cause, the accuracy of the results is further vitiated by the errors in the absolute values of the latent heats used in the calibration.

Heat of inversion. Typical time-differential temperature areas for the inversion of $K_2Si_4O_9$ are represented in Fig. 6. The value obtained for the

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[1] Plato: Z. physik. Chem., **55**, 721 (1906).

[2] Hare: Phil. Mag., **48**, 414 (1924).

[3] Goodwin and Kalmus: Phys. Rev., **28**, 1 (1909).
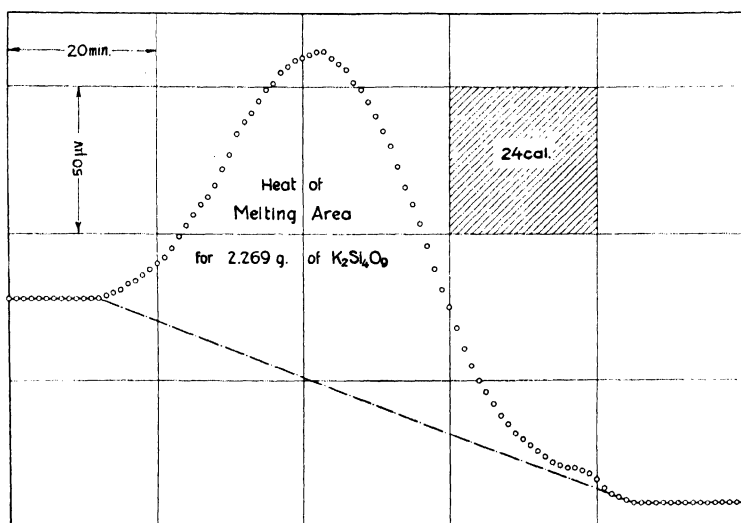
FIG. 5

Typical time-differential temperature melting curve of $K_2Si_4O_9$
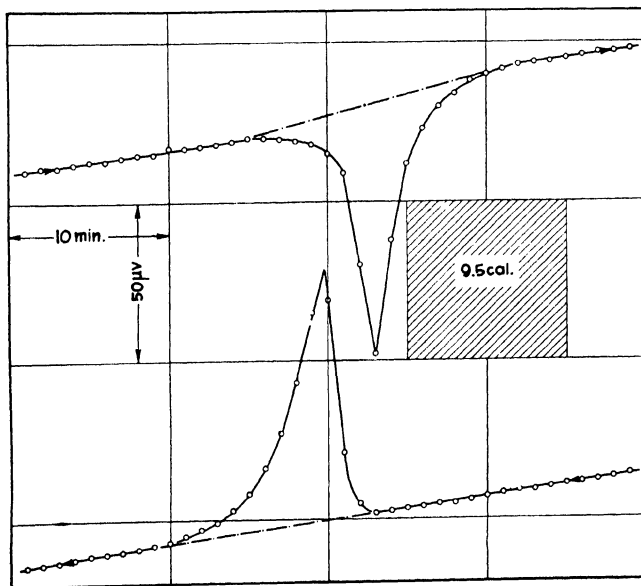
FIG. 6

Typical time-differential temperature inversion curves of $K_2Si_4O_9$

heat of inversion, as an average of four determinations, is 2.3 ± 0.3 cal. per gram (9.6 joules per gram).

Temperature-pressure-volume Relations

$K_2Si_4O_9$ is unusual among the silicates in that increase in pressure is accompanied by a lowering in the melting temperature of the compound. That is, the liquid state is denser than the crystalline state.

The initial slope of the melting curve, dt/dp at $p = 1$ bar, is $-60°$ per 1000 bars. The heat of melting is 146.5 joules (35 calories) per gram. Hence the volume change, Δv, on melting is

$$\Delta v = \frac{-0.060 \times 1465}{1038}$$

$$= -0.085 \text{ cm}^3/\text{g}.$$

where Δv denotes the specific volume of the liquid minus the specific volume of the crystals.

At 20°C (393° absolute) and atmospheric pressure (*vide supra*),

$$\Delta v = 0.419 - 0.428$$

$$= -0.009 \text{ cm}^3/\text{g}.$$

Therefore between 20°C and the melting point, 765°C or 1038° abs., the increase in volume of the crystals must be 0.076 cm³/g. more than that of the glass.

Since such a dilatation for the crystals appeared unreasonable it was thought that an inversion accompanied by a volume increase probably existed in this temperature interval. This whole temperature interval was carefully combed over and one inversion found at 592°C. It should be remarked that the method used, that of heating curves, is applicable only to transitions accompanied by a heat effect. The slope of this inversion curve, dt/dp, is 28° per 1000 bars, and the heat of inversion 9.6 joules (2.3 cal.) per gram. From these values we have

$$\Delta v = \frac{0.028 \times 96}{865}$$

$$= 0.0031 \text{ cm}^3/\text{g}.$$

where Δv denotes the specific volume of the high temperature form minus the specific volume of the low temperature form of $K_2Si_4O_9$.

There is then left 0.073 cm³/g. as the excess dilatation of the crystals above that of the glass in the 20° to 765° temperature interval. If we assume the dilatation of the glass to be negligible, then that of the crystals would average slightly in excess of 2×10^{-4} in the temperature interval $20° - 765°$ exclusive of the volume change on inversion. Comparison with other silicate compounds can not be made because dilatation data over extended temperature intervals are lacking except for SiO_2; the volume expansion coefficient of quartz in the interval from $20° - 573°$ is about one-third of the calculated expansion of $K_2Si_4O_9$. Above the inversion temperature, 573°, quartz has a negative dilatation which increases the discrepancy.

The character of the $K_2Si_4O_9$ inversion at 592° (atm. press.), its latent heat value and pressure coefficient are reminiscent of the quartz inversion at 573° for which the pressure coefficient is 21° per 1000 bars,[1] the heat of inversion 3 ± 1 calories per gram, and $\Delta v = 0.0032$ cm³ per gram.[2]

Crystalline $K_2Si_4O_9$ may then expand anomalously below its inversion to the high temperature form as does quartz. The parallelism in the characters of the inversion in quartz and this highly siliceous compound suggests a close relationship between the lattice structures of the two compounds. The lattice of $K_2Si_4O_9$ is probably a loosely bound one built on a framework of coordinated SiO_2 groups; this analogy with quartz would imply a similarity in the properties of $K_2Si_4O_9$ and quartz.

Stability of $K_2Si_4O_9$

Since it was found to be impracticable to obtain in all cases the stable phase relations of $K_2Si_4O_9$ directly from experiment, some of the phase boundaries must be obtained by indirect methods.

In order to do this it is necessary to investigate the binary system, $K_2Si_2O_5$–SiO_2, as the field of $K_2Si_4O_9$ lies between the fields of $K_2Si_2O_5$ and quartz. The phase boundaries of this system have been determined at atmospheric pressure as part of the more extensive binary system, K_2O–SiO_2.[3]

There are considerable calorimetric and dilatation data available for SiO_2 glass and quartz. There are, however, no data available for the remainder of the system other than phase equilibria information at 1 bar pressure and that contained herein on $K_2Si_4O_9$. The density at 25°C and the pressure-melting curve of $K_2Si_2O_5$ were therefore determined.

The density of crystalline $K_2Si_2O_5$ was determined by a pycnometer method using N-butyl ether as the displaced fluid. For the density of $K_2Si_2O_5$ glass we are indebted to Dr. H. E. Merwin, who obtained it by suspending the glass grains in a heavy liquid and measuring the density of the liquid with a Westphal balance. The results are: density of crystalline $K_2Si_2O_5$ at 25°C, 2.538; density of $K_2Si_2O_5$ glass at 25°C, 2.474. The difference in specific volumes of $K_2Si_2O_5$ glass and crystals at 25°C is therefore +0.01 cm³/g.

The pressure-melting slope of $K_2Si_2O_5$ was determined in the same way as was the pressure-transition curve of $K_2Si_4O_9$. The slope of the curve is positive though small, giving a rise of 3.5 ± 1°C in the melting temperature per 1000 bars increase in pressure.

The effect of pressure on the $K_2Si_2O_5$ liquidus was also investigated experimentally. A glass of composition 68.5 wt. per cent SiO_2 was crystallized and the liquidus point established after the same procedure used in obtaining the pressure-melting curve of $K_2Si_4O_9$. Owing to the difficulty of preparing these glasses accurately as to composition, since loss of potash takes place continuously during the preparation of them with consequent enrichment in silica content, and owing to the steep slope of the disilicate liquidus near the

[1] R. E. Gibson: J. Phys. Chem., **32**, 1197 (1928).
[2] R. B. Sosman: Int. Crit. Tables, **4**, 21.
[3] Kracek, Bowen, and Morey: Op. cit.

$K_2Si_4O_9$–$K_2Si_2O_5$ eutectic, it is very difficult to establish the pressure effect on the liquidus near the eutectic if this effect is small. Thus even a ten degree rise can easily be masked by a small error in composition. Therefore all that has been established in this region is that the pressure effect is relatively small, *i.e.* of the order found for the pure $K_2Si_2O_5$.

The thermodynamic quantities that must be evaluated and the necessary relations connecting these quantities have been presented elsewhere.[1] Furthermore, since the present data are such that exact quantitative results can not be evaluated and we are therefore limited here to a method of approximations
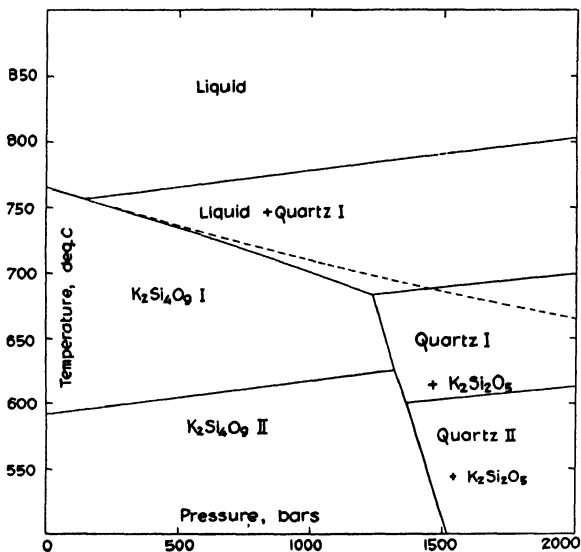
FIG. 7

Calculated temperature-pressure phase equilibrium diagram of $K_2Si_4O_9$. The dotted line is the metastable prolongation of the melting curve which was obtained experimentally. The numerals I and II after a compound denote the high- and low-temperature forms respectively

and general trends of the phase-equilibria boundary surfaces, only the results of such calculations are given here, and these are presented in a graphical form (Figs. 7 and 8).

In Fig. 7 are given the calculated phase-equilibria relations of $K_2Si_4O_9$. The dotted line represents the metastable prolongation of the melting curve of $K_2Si_4O_9$ which was realized experimentally and shown in Fig. 4. The numerals I and II after a compound refer to the high and low temperature crystalline form of the compound, respectively, thus Quartz I denotes the high temperature form of quartz.

Kracek, Morey, and Bowen found that at atmospheric pressure $K_2Si_4O_9$ melts congruently although the field $K_2Si_4O_9$ + Liquid in the system, $K_2Si_4O_9$–SiO_2, is small (see *A*, Fig. 8). At pressures above about 140 bars,

[1] R. W. Goranson: "Thermodynamic Relations in Multi-component Systems," Carnegie Inst. of Wash., Publ. No. 408, 152-161 (1930).

however, $K_2Si_4O_9$ melts incongruently to liquid and quartz I. At pressures above about 1250 bars $K_2Si_4O_9$ can no longer exist in stable equilibrium with liquid, and therefore can not form from melts above this pressure. Furthermore, since the solid $\rightleftarrows$ solid reaction

$$\text{Quartz} + K_2Si_2O_5 \rightleftarrows K_2Si_4O_9$$

probably can not be realized practically because of the very low velocity of the transformation, the final product of the melts crystallizing at pressures *above* 1250 bars would be $K_2Si_2O_5$ and quartz, and the presence of $K_2Si_4O_9$ crystals
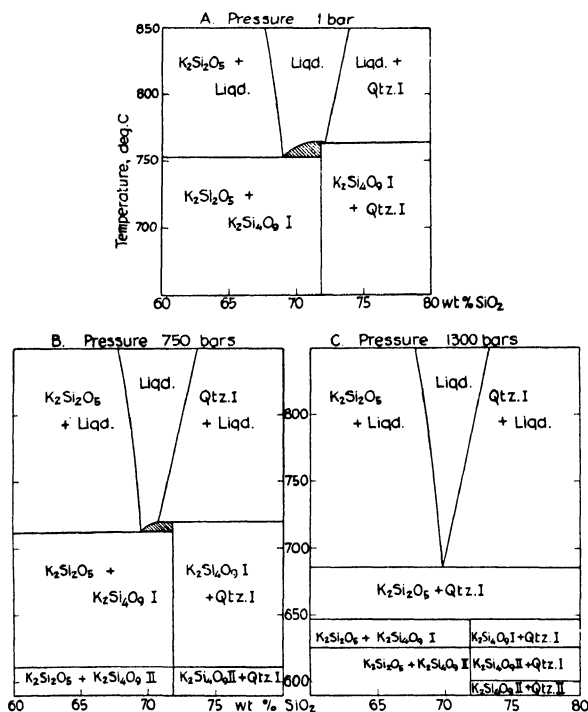
FIG. 8

Three cross-sections of a portion of the $K_2Si_2O_5$-SiO_2 phase diagram. *A* is the cross-section at 1 bar, *B* at 750 bars, and *C* at 1300 bars pressure. Note the progressive disappearance of the shaded area which represents the field of $K_2Si_4O_9$ + Liquid

in an agglomerate of unknown origin would indicate that the silicate solution had crystallized below this pressure.

The reaction

$$\text{Liquid} + \text{Quartz I} \rightarrow K_2Si_4O_9 \text{ I}$$
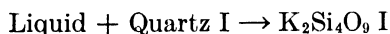
is relatively slow for in some samples which had stood at elevated temperatures for several weeks in bombs where water was used as a pressure medium and catalytic agent the crystalline products were $K_2Si_4O_9$, $K_2Si_2O_5$, and quartz.

In Fig. 8 are shown three cross-sections, *A*, *B*, and *C*, of a portion of the $K_2Si_2O_5$-SiO_2 phase diagram. *A* is a cross-section at 1 bar (metric atmosphere), *B* at 750 bars, and *C* at 1300 bars pressure.

A shows the congruent melting features of $K_2Si_4O_9$, the shaded area denoting the field, Liquid + $K_2Si_4O_9$. In *B*, $K_2Si_4O_9$ melts incongruently with a decrease in the Liquid + $K_2Si_4O_9$ field (shaded). In *C* the field, Liquid + $K_2Si_4O_9$, has disappeared completely, $K_2Si_2O_5$ and quartz forming a simple eutectic. Since the solid to solid reactions can probably not be realized, the compound $K_2Si_4O_9$ will be, for all practical purposes, non-existent in *C* which then would need to be modified to represent merely a simple eutectic relation between quartz and $K_2Si_2O_5$.

Summary

The phase relations of $K_2Si_4O_9$ were investigated experimentally to 3000 bars pressure (metric atmospheres). Values were also obtained for the slope of the $K_2Si_2O_5$ pressure-melting curve and for the heats of inversion and melting of $K_2Si_4O_9$ at atmospheric pressure. In these experiments the $K_2Si_4O_9$ solid→liquid phase boundary (metastable above about 140 bars pressure) was obtained in all cases. In consequence of the metastable region some of the stable phase relations had to be obtained indirectly. The results of such calculations were of necessity approximations because sufficient calorimetric and volumetric data were not available, but were, nevertheless thought to be of some interest and therefore included.

The results are tabulated below.

$K_2Si_4O_9$

Densities at $25°C$: crystals, 2.33₅; glass, 2.38₄.

Inversion curve: inverts at $592°C$ at atmospheric pressure; heat of transition is 9.6 joules per gram (2.3 calories); $dt/dp = 28°$ per 1000 bars; the calculated volume change on inversion, low → high, is +0.003 cm^3/g. These values are reminiscent of the quartz inversion.

Melting curve: $K_2Si_4O_9$ melts congruently at $765°C$ at atmospheric pressure; heat of melting is 146.5 joules per gram (35 cal.); the initial slope of the pressure-melting curve is − 60° per 1000 bars, *i.e.* an increase of pressure lowers the melting temperature at the rate of 60° for each kilobar increase in pressure. This boundary curve was realized experimentally to 3000 bars. The following phase equilibria relations were obtained indirectly: Above 140 bars pressure $K_2Si_4O_9$ melting becomes incongruent and the compound breaks up into quartz and liquid. Above about 1250 bars $K_2Si_4O_9$ can no longer exist in equilibrium with liquid but instead we have quartz and $K_2Si_2O_5$ forming a simple eutectic. Further, since the reaction

$$\text{Quartz} + K_2Si_2O_5 \rightleftarrows K_2Si_4O_9$$

probably can not be realized in practice, the presence of crystalline $K_2Si_4O_9$ in a mixture of unknown origin would indicate that the silicate solution had crystallized below about 1250 bars pressure.

$K_2Si_2O_5$

Density of crystals at $25°C$, 2.538; of glass at $25°C$, 2.474. The melting temperature is raised about $3.5°C$ for each kilobar rise in pressure.

Geophysical Laboratory,
Carnegie Institution of Washington.
November, 1931.

REDUCTIVITY OF HYDROGEN*

Part II.   Chloracetic Acid

BY G. RAYMOND HOOD AND HOMER C. IMES

Hood and Krauskopf[1] have shown that, in the electrolytic reduction of aqueous potassium chlorate, the efficiency of the reduction is a function of the cathodic overvoltage.   They measured the cathodic potentials of several metals against a reference electrode of "Absolute" potential 0.472 volt, at intervals throughout the course of the electrolysis, and plotting the cathode potentials against the reduction efficiencies, found that the efficiency of electrolytic reduction of aqueous potassium chlorate is negligible when the cathode potential exceeds 1.5 volt, and increases rapidly as the potential falls below this value.

In the present work, the investigation has been concerned with the electrolytic reduction of monochloracetic acid to acetic and hydrochloric acids, according to the reaction

$$CH_2ClCOOH + 2\,H \rightarrow CH_3COOH + HCl.$$

The apparatus and method have been described.[1]   The efficiency of the process with which we were concerned, i.e., the formation of HCl, was determined as before by gravimetric analysis.   During each experiment, 1080 coulombs passed through the cell.   It is evident from the equation that if the efficiency were 100%, $1080/193080 \times 143.34$ grams of AgCl should be recovered in the analysis.   The efficiency of the process is then equal to the weight of silver chloride found divided by 0.8018.

The chloracetic acid was of CP quality (Baker's) made up with redistilled water to approximately half-molal; the exact concentration was 0.529 molal. It gave no test for free chloride.

Potential-time curves for Fe, Ni, Cu, Pt, Mg, and Pb were observed over 3-hour periods during the electrolysis of approximately 250 cc. portions of this solution under a uniform current of 0.10 amp. and the efficiency of the concurrent reduction was determined.

The effect of electrolysis on the potential appears to be specific for each metal, but for a given cathode the *form* of the potential-time curves was closely reproducible; although the mean potential varied by as much as 0.1 volt from one experiment to another owing to our inability to reproduce the *initial* surface.

In general, the several metals exhibited variations in potential with time analogous to those shown in the electrolysis of 0.1 N sulfuric acid.   The magnitudes of the potentials were close to those exhibited in 0.1 N H_2SO_4, and thus considerably lower than are shown in 0.5 M $KClO_3$.

Potential-time curves of Fe, Cu, and Ni in 0.1 normal sulfuric acid, 0.493 molal potassium chlorate, and 0.529 Molal chloracetic acid are plotted in the figure; the curves for H_2SO_4 and $KClO_3$ being drawn from data of Hood and Krauskopf[1] and Hood.[2]

The mean cathode potentials of the several metals and the corresponding reduction efficiencies are given in the table. The current density was uniformly 0.0125 amp./sq. cm.

FIG. I
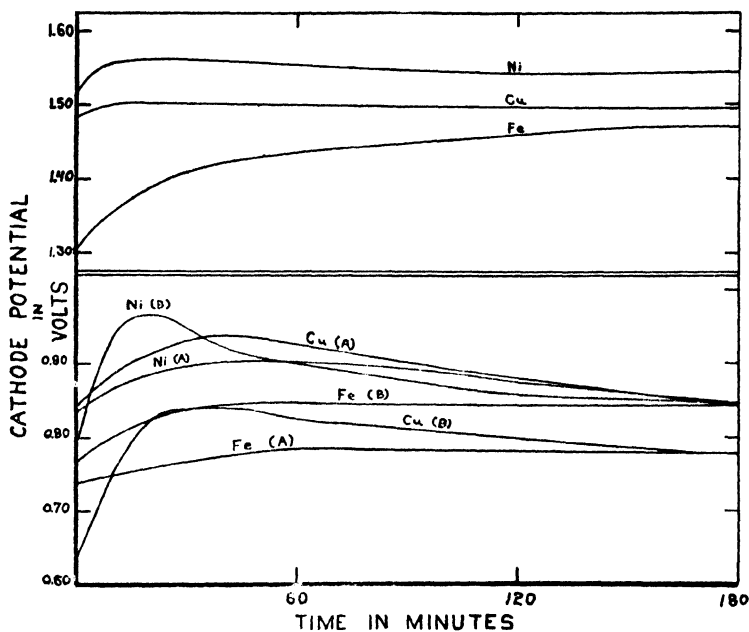
The curves in the upper half of the figure give the cathode potentials in 0.493 molal $KClO_3$ (Hood and Krauskopf); the curves marked (A) in the lower half of the figure give the cathode potentials in 0.1 normal H_2SO_4 (Hood); while the curves marked (B) give the potentials in 0.529 molal monochloracetic acid.

TABLE I

Cathode metal	Cathode potential	Current efficiency
Pt	0.805	10.4%
Cu	0.83	5.1%
Fe	0.845	13.0%
Ni	0.88	14.1%
Ni	0.94	15.8%
Cu	0.96	10.9%
Mg	1.13	18.8%
Pb	1.23	40.6%

[2] Hood: "Dissertation," University of Wisconsin (1930).

The data seem to indicate that as the potential of the cell test electrode-reference electrode increases, the efficiency of the process

$$CH_2ClCOOH + 2\ H \rightarrow CH_3COOH + HCl$$
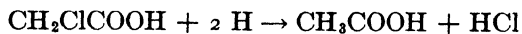
increases. The values obtained with a copper electrode are consistently low, but agree with the general conclusion in that the efficiency is greater at the higher potential.

These results appear to be in general accord with the hypothesis previously suggested.[1] The energy associated with the hydrogen atoms set free at the several electrodes must be greater in the order of the metals Pt, Cu?, Fe, Ni, Mg, and Pb; i.e., in the order of the metals producing increasingly greater overvoltages. In the reduction of chlorate, it appeared that only such hydrogen atoms could act as reductors as had an energy level corresponding to an overvoltage of 1.5 volt or less. In view of the fact that the process

$$KClO_3 \rightarrow KCl + 3\ O$$

involves a decrease in heat content of some 9800 calories; it was suggested that only slow or cold atoms would be effective as reductors. The transformation here considered involves a heat transfer of about 6000 calories, and consequently reduction could be effected by hydrogen atoms at a somewhat higher energy level. In addition, the competition for hydrogen atoms among the other reduction processes occurring simultaneously would tend to increase the efficiency at higher overvoltages (if we accept the hypothesis that this phenomenon arises in the slowness with which monatomic hydrogen is converted into molecules), by increasing the concentration of the reducing agent.

Summary

The efficiency of electrolytic reduction of aqueous monochloracetic acid into acetic and hydrochloric acids increases with the cathode potential throughout the range 0.80 to 1.25 volt.

Oxford, Ohio.

THE SORPTION OF WATER VAPOR BY CELLULOSE AND ITS DERIVATIVES

Part III. The Heat of Adsorption of Water Vapor by Cellulose Acetates*

BY P. T. NEWSOME AND S. E. SHEPPARD

The total heat of adsorption per gram of adsorbed vapor may be calculated from two adsorption isotherms within a restricted temperature range by means of equation (1).

Q (the total heat of adsorption in calories per gram of adsorbed vapor)

$$= \frac{RT_1T_2}{M(T_2 - T_1)} (\ln p_2 - \ln p_1) \qquad (1)$$

where p_2 and p_1 are the equilibrium pressures at the absolute temperatures T_2 and T_1 at which the adsorbent contains the same amounts of adsorbed vapor. M is the molecular weight of the adsorbed material.

Equation (2) is the Clausius-Clapeyron equation for the heat of condensation.

Q_1 (the heat of condensation in calories per gram)

$$= \frac{RT_1T_2}{M(T_2 - T_1)} (\ln P_2 - \ln P_1) \qquad (2)$$

where P_2 and P_1 are the saturation pressures at temperatures T_2 and T_1.

Equation (1) minus equation (2) gives the net heat of adsorption Q_2

$$= Q - Q_1 = \frac{RT_1T_2 (\ln p_2 - \ln p_1)}{M(T_2 - T_1)} - \frac{RT_1T_2 (\ln P_2 - \ln P_1)}{M(T_2 - T_1)}$$

$$= \frac{RT_1T_2}{M(T_2 - T_1)} \ln \frac{p_2}{P} - \ln \frac{p_1}{P} \qquad (3)$$

Hedges[1] found that the net heat of adsorption calculated from two adsorption isotherms by means of the last equation was equal to the heat of wetting of wool and silk by water.

Fig. 1 shows the moisture adsorption isotherms of a sample of cellulose acetate film base 39 per cent acetyl—(0.005 inch thick) at 30, 40 and 50°C. plotted as a function of the relative vapor pressure p/P. Direct application of equation (3) to these curves gives the net heat of adsorption.

Fig. 2 gives the same data plotted as a function of the absolute water vapor pressures. Direct application of equation (1) to these curves gives the total heat of adsorption.

The same piece of film base was used in obtaining all three isotherms on the silica spring balance.[2] After measuring one isotherm, the adsorbed water was

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removed by evacuation and the next adsorption curve determined. The sample had previously been carried through several adsorption-desorption cycles to eliminate certain small changes in adsorptive capacity which had been found to occur in the first three cycles.

Table I shows the data for the total heats of adsorption over the range 30 to 40°C. and 40 to 50°C.

FIG. I
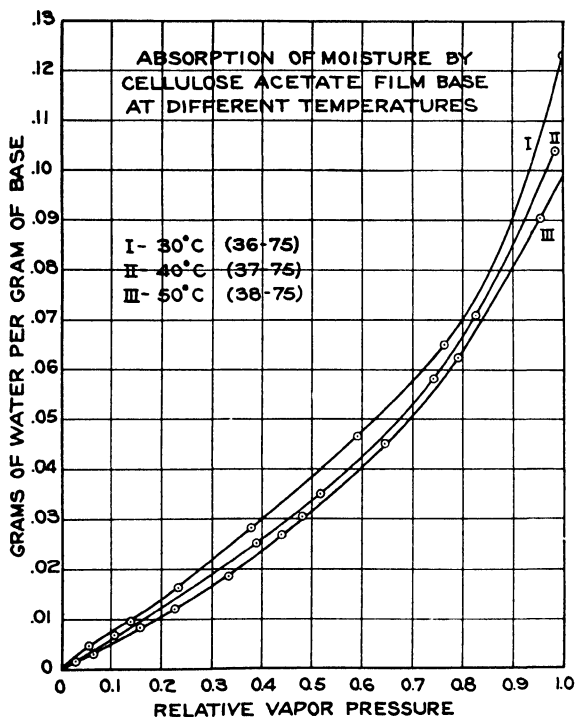
TABLE I

Heat of Adsorption of Moisture by Cellulose Acetate Film

Moisture Content	Equilibrium Pressures (mm. Hg at 0° C.)			Total Heat of Adsorption (cals. per gram of water)	
	30° C.	40° C.	50° C.	30 to 40° C.	40 to 50° C.
1	4.3	9.1	17.0	785	697
2	9.0	17.3	32.9	684	717
3	13.1	24.9	43.9	672	633
4	16.6	31.4	54.3	667	611
5	19.9	37.0	63.8	649	608
6	22.9	41.6	71.3	625	601
7	25.4	45.3	77.7	606	602
8	27.3	48.4	83.2	599	604
9	28.7	51.0	87.9	602	607
10	29.9	53.5	92.3	609	609

$$\text{Total heat of adsorption} = Q = \frac{RT_1T_2(\ln p_2 - \ln p_1)}{M(T_2 - T_1)}$$

Over the range 30 to 40°C., $Q = 2411 (\log p_2 - \log p_1)$

Over the range 40 to 50°C., $Q = 2570 (\log p_2 - \log p_1)$

MOISTURE ADSORPTION ISOTHERMS
OF CELLULOSE ACETATE SHEET.

● AT 30°C.
▲ " 40°C.
✕ " 50°C.

WATER VAPOR PRESSURE (mm. Hg AT 0°C.)
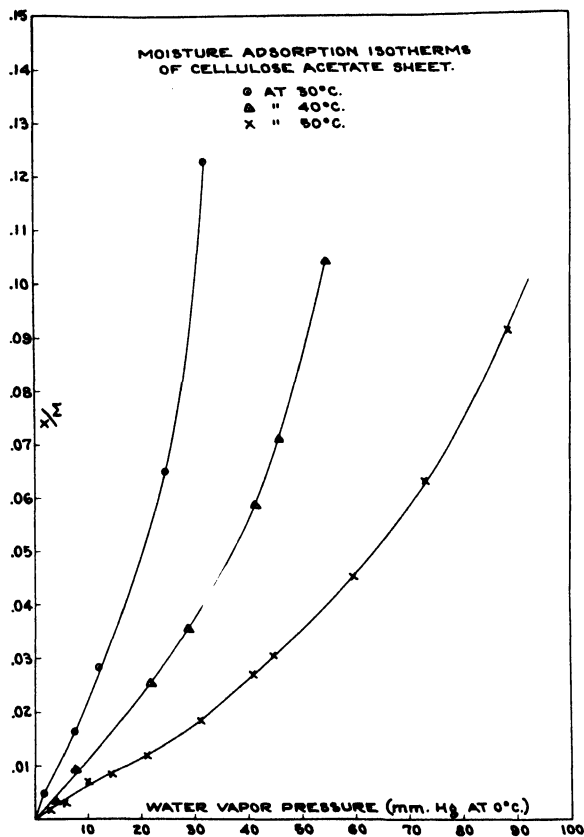
Fɪɢ. 2

The 2nd, 3rd and 4th columns give the equilibrium pressures at which the film contains the various amounts of moisture shown in column 1. These pressures were interpolated from the curves shown in Fig. 2.

Fig. 3 shows the heats of adsorption plotted as a function of the initial moisture content of the film. These are the curves of differential heat of adsorption.

In both curves the heat of adsorption is greatest for the first small amounts of adsorbed water and then rapidly decreases to values not far above the heats of condensation, 577 calories at 35°C. and 572 calories at 45°C.

The differential heats of adsorption of moisture by cellulose acetate film base were experimentally determined by means of the apparatus shown in Fig. 4.

In preliminary experiments, the amount of water adsorbed was determined by observing the drop in level of the liquid water in the calibrated capillary tube, G. This tube was maintained at a constant temperature of
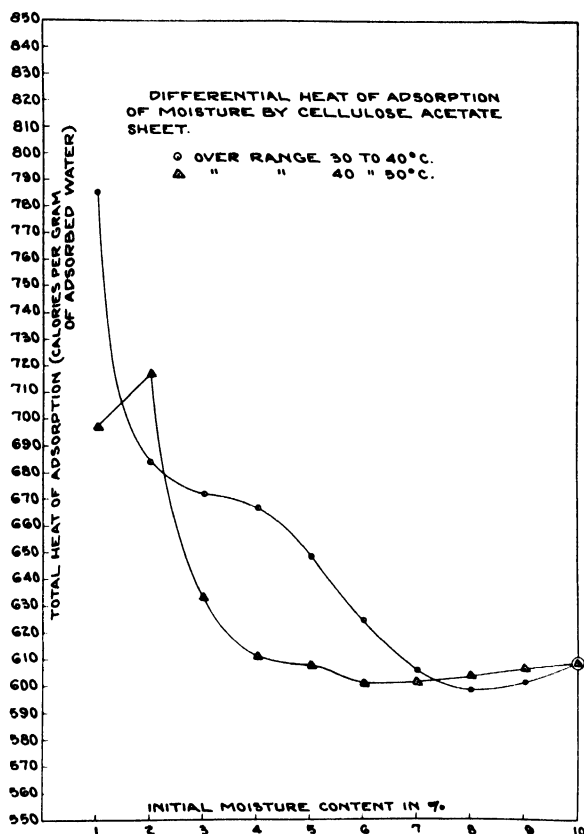
FIG. 3

20°C. In later experiments, however, it was found easier and more accurate to obtain these values from a previously determined adsorption isotherm.

The calorimeter was maintained at a temperature of 25°C. in a water thermostat. The sample of film base cut in small pieces was enclosed in the bulb, A, within the calorimeter. The calorimeter is fitted with a mercury-sealed stirrer (60 to 150 r.p.m.), a Beckmann thermometer, and a calibrated resistance heater. The heat capacity of the calorimeter was 125 calories.

The rise in temperature and the corresponding equilibrium pressures were observed on successive additions of water, time being allowed for the attainment of equilibrium and readjustment of the calorimeter temperature at each addition of water.
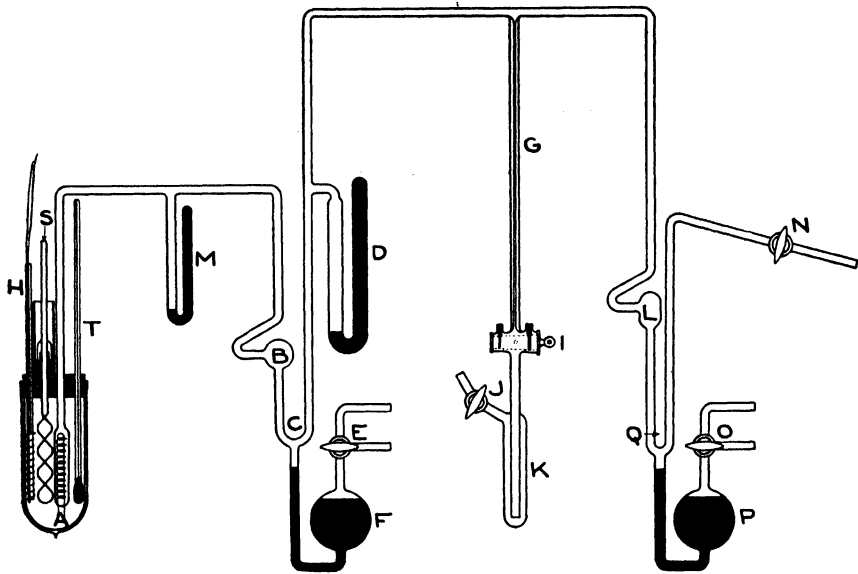
FIG. 4
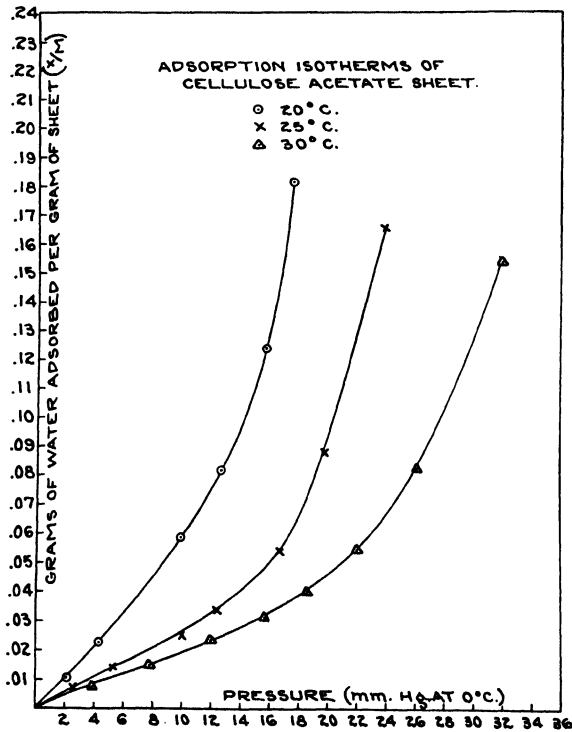
FIG. 5

Table II shows the data for the heat of adsorption of moisture by a cellulose acetate film base at 25°C. The acetyl content was 38 per cent and the thickness, 0.005 inch. The table shows the initial and final moisture contents, the temperature rise ΔT, the integral heats of adsorption, H (total heat liberated per gram of film base), and the differential heats of adsorption, Q, per gram of adsorbed water. The latter decrease rapidly with increasing initial moisture content.

TABLE II

Heat of Adsorption of Moisture by Cellulose Acetate Film at 25°C.

Moisture Content gm/gm base		Grams water Adsorbed per gram Film	T(°C.) for 2.564 gm. Film	Total Heat Liberated per gram Film	Q
Initial	Final				
0	0.0040	0.0103	0.063	3.2	794
0.0040	.0079	.0100	.064	6.4	827
.0079	.0115	.0092	.045	8.7	(630)
.0115	.0198	.0213	.126	15.0	765
.0198	.0300	.0262	.148	22.5	731
.0300	.0435	.0346	.183	31.7	683
.0435	.0775	.0872	.407	52.2	604

Fig. 5 shows the adsorption isotherms at 20, 25 and 30°C., the heats of adsorption at 25°C. being calculated from the isotherms at 20 and 30°C., by means of equation (1) and compared with the experimental values at 25°C. just shown in Table II.

Fig. 6 shows the comparison between the experimental and the calculated values. The experimental heats of adsorption were plotted in two ways, *i.e.*, either (1) as a function of the initial moisture contents, or (2) as a function of the average moisture contents between steps. The latter curve brings the experimental heats of adsorption a little nearer the calculated curve, but the calculated values are still much higher than the experimental. Both calculated and experimental values fall rapidly with increase in initial moisture content and appear to approach the heat of condensation of water.

Measurements were also made of the heat of adsorption of water vapor by fibrous cellulose triacetate (44.8 per cent acetyl). On account of the bulkiness of the material, only one-half gram could be charged into the adsorption bulb. As a result, only a small amount of water was adsorbed and the heat liberated was correspondingly small. The differential heats were not obtained since small temperature changes could not be accurately measured, but the integral heats, starting in each case with zero moisture content were obtained as shown in Table III. This table shows the amount of water adsorbed (x/m) at the relative vapor pressure (p/P) and the corresponding total amount of heat (H) liberated by the adsorption of x/m grams of water.
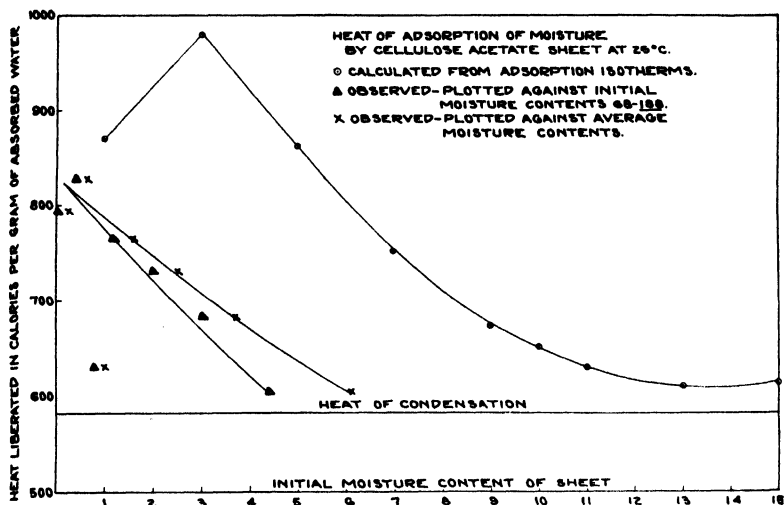
FIG. 6

TABLE III

Heat of Adsorption of Moisture by Cellulose Triacetate at 25°C.

p/P	x/m	H	p/P	x/m	H
0.073	0.0038	4.3	0.466	0.0296	17.6
.206	.0113	7.9	.633	.0410	24.8
.348	.0198	13.1	.637	.0413	27.4
.360	.0205	13.8	.750	.0515	33.0
.465	.0280	18.4			

Fig. 7 shows a comparison of the integral heat of adsorption curves of cellulose "diacetate" and cellulose triacetate, along with a theoretical curve based on pure capillary condensation.

This graph shows that the total heat liberated in the adsorption of moisture by the triacetate is less than that liberated in the adsorption of the same amount of water by the diacetate, and also is nearer to the capillary condensation curve.

This substantiates a theory previously deduced[3] from numerous adsorption experiments with cellulose and cellulose acetates, that there are two main factors influencing the adsorption of water. First, water is initially adsorbed by the free hydroxyls in the cellulose material, and second, further adsorption of water consists mainly in the condensation of water vapor into the voids of the cellulose material. Thus, adsorption by a completely acetylated cellulose with no free hydroxyls is mainly a process of condensation in capillary spaces, and the heat liberated should approach very near to the capillary condensation curve.

These deductions, of course, are only approximate and are applied only to this particular study. With a partially esterified cellulose acetate or with any other solid there will be a certain amount of heat liberated, because of adsorption at the surface, regardless of the chemical nature of that surface. If adsorption from the vapor were a pure condensation process, then there should be no heat of wetting or net heat of adsorption. Even with the triacetate
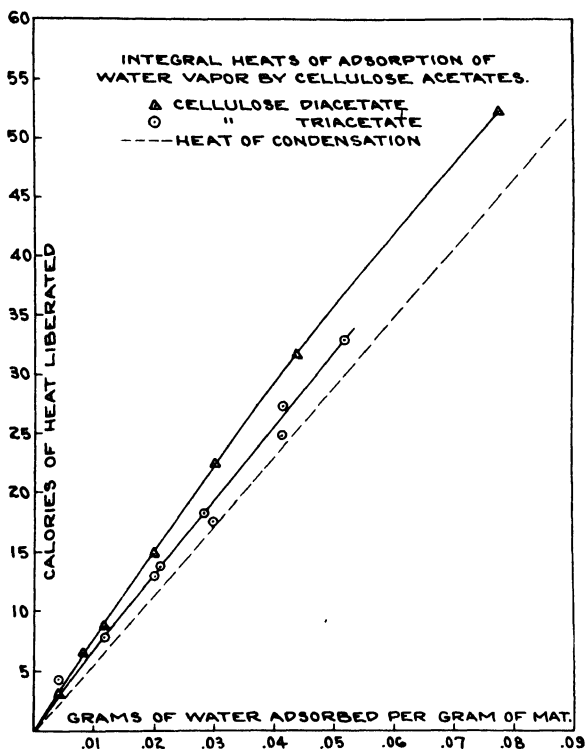
FIG. 7

above, there is a considerable net heat at low initial moisture contents. Barratt and Lewis[4] found that the heat of wetting of a sample of pure cotton containing 5.1 per cent moisture content of the cotton increases from 5 to 20 per cent in this operation; we have a heat of wetting, or a net heat of adsorption per gram of water of 24 calories.

Further, in the condensation of water vapor into capillary spaces already lined with adsorbed water, there will be a certain amount of heat liberated by reduction in liquid surface as the pores fill up. This was sufficient to explain all of the net heat of wetting of silica gel by water (20 calories) as observed by Patrick and Grimm.[5]

Polanyi and Welke[6] calculated the differential heats of adsorption of sulfur dioxide on charcoal from two isotherms at 0° and 5.3°C. There was a sharp minimum at a low value of x/m where the heat of adsorption was less than the

heat of condensation.   The differential heat of adsorption of water on charcoal gives a rising curve with the heat of adsorption below the heat of condensation of water.

When the heat of adsorption of a substance is smaller than its heat of condensation, the substance is adsorbed more at a higher temperature and at the same relative vapor pressure.

The latter phenomenon was observed by Urquhart and Williams[7] for cotton above 80 per cent relative humidity over the temperature range 60 to 110°C.

Bibliography

[1] J. J. Hedges: Trans. Faraday Soc., **22**, 178 (1926).

[2] *Cf.* S. E. Sheppard and P. T. Newsome: J. Phys. Chem., **33**, 1317 (1929).

[3] *Cf.* (2), also J. Phys. Chem., **34**, 1158 (1930).

[4] Thos. Barratt and J. W. Lewis: J. Text. Inst., **13**, T113 (1922).

[5] W. A. Patrick and F. V. Grimm: J. Am. Chem. Soc., **43**, 2144 (1921).

[6] M. Polanyi and K. Welke: Z. physik. Chem., **132**, 371 (1928).

[7] A. R. Urquhart and A. M. Williams: J. Text. Inst., **15**, T559 (1924).

Rochester, N. Y.,
November 18, 1930.

THE THERMAL DECOMPOSITION OF TETRAMETHYLLEAD*

BY J. H. SIMONS, R. W. McNAMEE, AND CHARLES D. HURD

Several noteworthy experiments on the pyrolysis of metal alkyls have been announced in recent years. That of Paneth and Hofeditz[1] is best known since these investigators found that some active body, capable of removing lead mirrors, was produced as tetramethyllead was heated. Paneth assumed that the active body was free methyl radical. The identity of the decomposition products was not studied. Such information would be of importance, especially in view of the assumption of free radicals made by Rice,[2] by Taylor and Jones,[3] and others in postulating the mechanism of certain simple organic reactions.

Experiments on the thermal decomposition of ethylsodium in the solid phase have been made by Schorigin[4] and by Carothers and Coffman.[5] Geddes and Mack[6] determined the products formed from tetraethylgermanium and found its rate of decomposition. Taylor and Jones decomposed diethylmercury, tetraethyllead, and dimethylmercury; but did not analyze the products completely, as their interests were on the effects of the presence of these substances upon the reactions of ethylene. Jones and Werner[7] decomposed various alkyl derivatives of mercury and lead in acetic acid solution.

The purpose of the present work was to decompose the vapors of tetramethyllead by a flow method under conditions similar to those used by Paneth and Hofeditz and to compare the products so formed with those obtained by a static method in which the experimental conditions of heating were greatly different. In the flow method the vapor of tetramethyllead was drawn through a short heated region at a very high velocity after which it was rapidly cooled. The pressure was kept below 2 mm. of mercury. It was hoped that by this method the initial active substances could be removed to a cold part of the tube before their readjustment into stable compounds. The conditions used duplicated those of Paneth and Hofeditz with the exception that no carrier gas was used. When hydrogen was used for this purpose, a lead mirror was readily removed by the active substance. In the static method the material was heated for a considerable period of time in sealed pyrex tubes. Each bulb contained sufficient of it to give a pressure of an atmosphere or two at the temperature used. The temperatures varied between 265°-620°, as contrasted with 550°-820° in the flow method. Furthermore, aside from tem-

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[1] Paneth and Hofeditz: Ber., **62**, 1335 (1929).
[2] Rice: J. Am. Chem. Soc., **53**, 1959 (1931).
[3] Taylor and Jones: J. Am. Chem. Soc., **52**, 1111 (1930).
[4] Schorigin: Ber., **43**, 1931 (1910).
[5] Carothers and Coffman: J. Am. Chem. Soc., **51**, 588 (1929).
[6] Geddes and Mack: J. Am. Chem. Soc., **52**, 4372 (1930).
[7] Jones and Werner: J. Am. Chem. Soc., **40**, 1257 (1918).

perature differences the pressure was some five hundred times greater, the time of contact was thousands of times greater, and the formation of the final products took place in the same region where the active substances were created so that the readjustment must have occurred in the presence of considerable quantities of both the original substance and the reaction products.

Great care was exercised to insure the absence of impurities, especially oxygen and organic iodides, which Paneth indicated prevented the removal of the mirrors. This caution was also based upon the work of Geddes and Mack, who found that 0.1% of oxygen greatly increased the rate of the decomposition tetraethylgermanium.

Experimental Procedure

The tetramethyllead was prepared from methylmagnesium iodide and lead chloride in the usual way. It was purified by distillation, the distillate coming over between 48-50° at 100 mm. To remove any residual iodides, the distillate was left for a week in contact with freshly precipitated silver oxide. Then it was redistilled, and the distillate dried with anhydrous calcium chloride. It was distilled into the apparatus and the retained gases boiled out. The entire apparatus was pumped out to a pressure of 1×10^{-6} mm. of mercury or less before the flow method was used, and the bulbs were pumped out to a similar vacuum before the tetramethyllead was distilled into them.
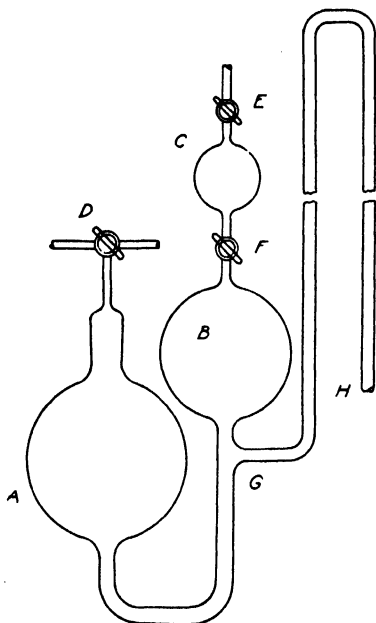
Fig. 1

Flow Method. The apparatus used consisted of a high vacuum bench with the necessary pumps, McLeod gauge, etc. For the flow method of decomposition the tetramethyllead was contained in a small bulb, which could be immersed in cooling baths. This was connected first through a U-tube (made of 6 mm. pyrex tubing) which was heated by immersion in a molten salt bath, then through a second U-trap which was cooled by a solid carbon dioxide and acetone bath to remove any undecomposed material carried over, and finally to both the high vacuum pumping system and the apparatus shown diagrammatically in Fig. 1. In this piece of apparatus there was sufficient mercury to fill both the bulbs C and B and at the same time not to expose the lower outlet of bulb A. One outlet of the threeway stopcock was connected to a vacuum pump and the other to a source of compressed air. Connection to the rest of the apparatus was made at H. A had a volume of 1000 cc; B, 500 cc; and C, 100 cc. The height of the tube between G and H was 100 cm. to hold the mercury in place.

After the apparatus had been pumped out and the residual gas boiled out of the tetramethyllead, the appropriate temperature baths were put into place. The container for the tetramethyllead was cooled to about $-20°$ with ice and salt. The temperature of the hot bath was controlled by a Bunsen burner and was measured with a chromel-alumel thermocouple. The U-tube was immersed in the heated liquid to a depth of 5 cm. or less. The stopcock, which separated the container from the rest of the apparatus, was not opened. By pumping the air out from above the mercury in A, the bulbs C and B were emptied; and when G was exposed, the gas from the decomposition filled them. This gas was trapped in C by allowing air to enter A and so forcing the mercury up into B after which stopcock F was closed. By pulling the mercury down again another quantity of gas was trapped in B, which was in turn forced into C. By repeating this operation C could be filled to any desired pressure. It took 200 to 300 of these operations to fill the bulb (100 cc.) with gas at atmospheric pressure. The gas so obtained was forced through E into a gas pipet and was analyzed.

The opening of the large volume of empty space in B to the rest of the apparatus drew the gas through the heated region at very high velocity. The time of contact was estimated by varying the time that the opening at G was made and determining the shortest time necessary to fill B. From this and the relative volumes of B and the heated region an approximate value of the contact time could be calculated. In these experiments it was judged to be less than 0.001 second.

For temperatures above 600° the first U-tube was replaced by a horizontal piece of quartz tubing. This was heated by a small electric furnace built around it. The thermocouple junction was placed in the center of the furnace next to the outside of the quartz tube. Temperature measurements made in this manner or those made by having the thermocouple junction in the molten salt bath give the temperature of the outside of the tube. This is somewhat higher than that of the gas which is rapidly streaming through the inside of the tube. The values so obtained can, however, be used for comparisons.

Static Method. The bulbs used in the static method were of about 100 cc. capacity and had capillary tips on both ends. One of these was sealed shut and the other sealed to a manifold, which connected through a stopcock to the container of tetramethyllead. After the evacuation a visually determined quantity of the liquid was distilled into the bulbs. They were then sealed off and weighed. After being heated in a furnace for a given length of time, the gases contained in them could be forced into the analysis apparatus by the following means. The capillaries were scratched with a file. Over one of them was placed a rubber tube filled with mercury and connected to a mercury reservoir. The capillary was then broken while it was inside the rubber connection. As the tube contained approximately enough of the original substance to produce one atmosphere pressure at room temperature, there was very little rush of the gas out of the bulb or of mercury into it. A

short rubber tube on the upper capillary connected it to the analysis apparatus. Breaking this capillary enabled the gas to be forced out by means of the mercury with very little air introduced.

The weight of the cleaned bulb and the capillary tips subtracted from the weight of the bulb before it was opened gave the weight of the tetramethyllead decomposed.

The analysis were made by a modified Orsat apparatus with the method described by Hurd and Spence.[1]

Results

The results of the flow method are given in Table I and those of the static method in Table II. In runs 7 to 11 of Table II, both tarring and carbonization were observed. Runs 11 and 14 showed diminishing carbonization and no tarring. The deposits in runs 15 to 17 was a sputtered film of lead, loosely held, and easily dissolved in mercury. In these three runs very little carbonization was observed.

As the initial temperature at which decomposition took place in the bulbs was 265°, as contrasted to the initial temperature of 425° which was required to obtain a deposit in the flow method, it is evident that corresponding temperatures in the latter are about 150° higher than in the former. There are two possible explanations for this difference. One is that the rapidly moving gas has not come into temperature equilibrium with the walls of the tube, and the other is that the temperature at which the corresponding reactions take place is higher due to the much shorter time of contact and lower pressure.

A bulb held at 265° for twenty hours still contained tetramethyllead, as was shown by the formation of liquid on cooling to room temperature. This showed the reaction at this temperature to be very slow. At 550° the reaction was complete in less than ten minutes.

TABLE I

Decomposition of Tetramethyllead by Flow Method

Run	1	2	4	4	5
Temperature of tube °C	550	550	700	700	820
Average Pressure, mm. of Hg.	0.5	1.5	2.0	1.7	2.0

Percentage by Volume of Gaseous Products

Acetylene	0.1	0.5	0.0	0.0	0.0
Isobutylene	1.8	5.1	0.3	0.8	0.3
Propylene	0.8	1.5	0.3	0.4	0.4
Ethylene	1.8	2.5	2.8	2.4	18.4
Hydrogen	2.4	4.9	0.1	14.6[a]	9.2
Methane	10.4	24.9	31.0	33.2	47.8
Ethane	82.8	58.7	65.5	49.8	23.9

[a] Hydrogen was added to the tetramethyllead before decomposition, thereby increasing the percentage of hydrogen in this case.

[1] Hurd and Spence: J. Am. Chem. Soc., **51**, 3353 (1929).

TABLE II

Decomposition of Tetramethyllead by Static Method

Run	7	8	9	10	11	12	13	14	15	16	17
Temperature, °C	265	295	315	340	365	395	440	460	550	550	620
Pressure, mm. Hg.	820	1240	1240	1330	1900	1900	800	—	—	700	1000
Contact time, hours	25.0	25.0	7.5	7.0	4.0	4.0	0.5	0.33	2.0	0.16	0.16
Weight of Pb(CH₃)₄, g.	0.26	0.30	0.35	.0.43	0.50	0.40	0.14	—	—	0.12	0.11
Volume of gas cc. at 760 mm.	60	84	90	120	135	120	40	—	—	40	40
Volume of bulb, cc.	110	100	110	130	120	115	100	—	—	120	100
Moles of gas per mole Pb(CH₃)₄	2.6	2.9	2.8	3.1	3.0	3.3	3.2	—	—	3.6	3.8

Percent by Volume of Gaseous Products

	7	8	9	10	11	12	13	14	15	16	17
Acetylene	2.5	—	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0
Isobutylene	5.3	4.5	1.3	1.9	2.1	2.2	1.2	1.2	0.7	0.5	0.6
Propylene	3.0	2.1	1.6	1.9	2.3	2.8	2.3	2.3	2.8	0.5	1.0
Ethylene	2.0	2.5	1.7	2.0	1.8	1.5	2.3	5.0	26.2	25.6	25.5
Hydrogen	0.0	0.0	1.1	0.5	0.3	0.7	3.5	9.2	22.2	28.2	25.1
Methane	65.1	68.9	78.5	86.1	82.2	74.2	51.9	49.5	28.7	22.6	27.7
Ethane	21.7	22.9	15.7	7.8	11.6	18.5	38.9	33.0	19.2	22.6	19.9

Probably the most outstanding difference in the course of the low temperature reaction from that of the high temperature reaction is carbon formation. The appearance of the firmly attached black mirror of carbon and lead which resulted in the former case was quite different from the loosely-held, sputtered, gray surface of lead (without carbon) which was deposited at higher temperatures. The former would not distill away when heated *in vacuo*, nor would the mirror disappear when it was subjected to the action of methy radicals in the manner of Paneth and Hofeditz. Furthermore, the mirror was not soluble in mercury. In contrast, the sputtered lead mirror did all three of these things.

The unusual production of carbon at the lower temperatures but not at the higher and also the change in the reaction products with change in temperature point to the conclusion that the decomposition takes place by two separate sets of reactions. One of these is comparatively slow and takes place at the lower temperatures. From the closely adhering character of the deposit, this is judged to be a wall reaction. The other is a fast reaction which takes place at the higher temperatures and forms the loosely held sputtered lead deposit. From the similarity of this deposit to that reported by Geddes and Mack[1] in the decomposition of tetraethylgermanium, it is assumed that this is a homogeneous reaction. They concluded that their reaction was at least 98% homogeneous.

Carbon formation was prominent in runs 7 to 11 where the temperature ranged between 265-365°. In these runs methane and ethane comprised 87-94% of the gaseous products and the olefines ethylene, propylene and isobutylene 10-5% of the products. All five of these hydrocarbons are stable at temperatures[2] 265-365° in quartz or pyrex tubes. At least, under these conditions there is no appreciable carbon formation. The carbon which was noticed from tetramethyllead has its origin from some source other than the paraffins and olefins in the gaseous products.

Discussion

Previous workers have postulated that the tetramethyllead molecule in its decomposition formed a lead atom and hydrocarbon fragments. Paneth and Hofeditz have considered these fragments to be free methyl radicals. Whether such is the case or not is irrelevant to the present discussion. It is convenient, however, to retain the term radical in this connection, despite a possible error in so doing.

In order to explain the products formed, it will be assumed that at the lower temperatures a slow reaction takes place in the condensed phase on the walls of the vessel, and at the higher temperatures the reaction is rapid and homogeneous in the gas phase. Because the latter is rapid, it consumes the tetramethyllead before any considerable quantity has reacted according to

[1] Loc. cit.

[2] Hurd: "The Pyrolysis of Carbon Compounds," 50-79 (1929).

the former reaction. Only the products methane, ethane, ethylene, and hydrogen will be considered, assuming the other products formed in relatively small quantities to be due to side reactions.

When the decomposition occurs on the walls of the vessel in a condensed phase, the molecules of the reacting substance are packed tightly together. Under these conditions the methyl radicals, as they are disrupted from the lead atom, are in close contact with other tetramethyllead molecules and so can extract hydrogen from them to form methane in quantity. By coming in contact with other methyl radicals on the walls, they can form ethane. As the temperature is raised, the reaction proceeds more rapidly, and the activity of the methyl radicals increases to form even higher proportions of methane. This trend is seen in runs 7, 8, 9, and 10. Lower temperatures in a condensed phase would also tend to favor side reactions. The deposit left on the wall would consist of lead, carbon, and tarry hydrocarbons. As the temperature is further raised, the concentration of methyl radicals increases; and this gives greater opportunity for their combination to form ethane. This trend is seen in runs 11, 12, and 13. At 550°, runs 15 and 16, the high temperature reaction begins to set in. The methyl radicals are now released in the gas phase and have the opportunity of a variety of reactions. In a two-body collision between two methyl radicals we would expect ethylene and hydrogen to be formed, one or both of which would be highly activated. As a matter of fact, the production of ethylene and hydrogen was found to be strikingly increased, and both were present in approximately equivalent amounts. A three-body collision in the considerable gas pressure in the bulb is also highly probable. Two methyl radicals meeting in a three-body collision could form ethane by releasing the energy of combination to the third body. Even at the higher temperatures there is probably some of the low temperature wall reaction taking place to produce some of the methane. Methane could also be formed in the gas phase by a reaction of the methyl radicals with the hydrocarbons present or with molecular hydrogen.

In the flow method of decomposition, there is an entirely different set of conditions. The active methyl radicals are preserved in a comparatively stable condition, since they are rapidly removed from the heated region. As Paneth and Hofeditz were able to detect the active substance in their experiments as long as 0.026 second after its formation at a gas pressure of 2 mm. of mercury, it must be relatively stable. In these experiments it remained in the heated region less than 0.001 second. Not having sufficient energy to form ethylene and hydrogen by a two-body collision, it reacts to form ethane by a three-body collision or wall reaction. Actually, a high proportion of ethane was found in these experiments. At 550° a carbonaceous deposit indicated a wall reaction which was similar to that formed in the tubes at lower temperatures and accounts for the methane content. Methane could also be formed by reaction between the methyl radicals and hydrogen or hydrocarbons present. That the methyl radicals require more energy to form ethylene and hydrogen than to form ethane is seen in the increasing proportion of ethylene with increased temperature.

A comparison of runs 1 and 2 which were at the same temperature, but at different average pressures shows that at the lower pressure considerably higher percentage of ethane is formed and lower percentages of methane, ethylene, and hydrogen. At the lower pressure the methyl radicals have a greater mean free path and so leave the heated region and the carbonaceous deposit on the wall more readily. Furthermore, they have less opportunity to meet tetramethyllead molecules in the heated region. This is in agreement with our suggestion that they would combine in the cold portions of the tube to form ethane. Run 4 was at the same temperature as run 3, but in the former a small amount of hydrogen was allowed to leak into the tetramethyllead container. It is seen that this reduced the percentage of ethane with a corresponding gain in the amount of methane. This indicates a reaction between the methyl radical and hydrogen.

Lead Mirrors. These experiments suggest the reason for the difficulties encountered in the removal of lead mirrors by methyl radicals, when the mirrors are prepared by pyrolyzing tetramethyllead. Unless sufficiently elevated temperatures are taken, carbon, which is not removed by methyl radical, is formed in the mirror. If satisfactory temperatures are used, quartz tubing is essential since pyrex glass would collapse under the reduced pressure in the apparatus. To be sure metallic mirrors which are not contaminated with carbon can be readily formed by vaporizing the metal and condensing it on the glass surface, but this does not concern us here. The presence of traces of oxygen may accelerate the decomposition on the wall, and this explains why its complete removal is necessary.

Correlation of Existing Data. Paneth and Hofeditz report that the decay of the methyl radical is linear with time after its formation, suggesting a reaction which is first order with respect to the radicals. In line with the above work this can be explained in the following manner. In their experiments the concentration of hydrogen was very much greater than that of the methyl radicals. This would give but little opportunity for collisions between methyl radicals to form either ethane or ethylene and hydrogen, reactions which would be second order with respect to the methyl radicals. A reaction between the methyl radicals and molecular hydrogen to form methane and active hydrogen atoms would, however, be first order with respect to the radicals, thereby satisfying the conditions. When a hydrocarbon, instead of hydrogen, serves as atmosphere for the methyl radicals, Rice[1] has found the decay to be second order with respect to the radicals. This suggests that the methyl radicals do not react with hydrocarbon molecules in the cold, an assumption which is in agreement with the results and hypotheses presented in this paper.

In the decomposition of ethylsodium, Carothers and Coffman[2] found that the chief products were ethylene, hydrogen, and ethane in the ratio of 8, 4, and 1 respectively. Ethylsodium is a salt-like compound[3] with a very low

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[1] F. O. Rice: Paper presented before the Physical Chemical Division of the American Chemical Society at the Buffalo meeting, September, 1931.

[2] Loc. cit.

[3] Hein and Schramm: Z. physik. Chem., **151 A**, 234 (1930).

vapor pressure and, therefore, the decomposition takes place in the solid phase. If the compound has an ionic crystal lattice, which its properties indicate, the sodium ion is as close to the beta carbon in any one of the adjacent ethyl ions as to the alpha carbon. This physical condition would facilitate the disruption into ethylene and sodium hydride in the manner which these authors postulate as the major reaction. They obtained indications of sodium carbide as a product of the pyrolysis. In explaining this and also the formation of ethane, they have postulated a mechanism which assumed as intermediate products $NaCH_2CH_2Na$ and $Na_2CHCHNa_2$. In the ionic crystal lattice these should be written $2\ Na^+ + CH_2CH_2^{--}$ and $4\ Na^+ + CHCH^{----}$. It seems highly improbable that doubly and quadruply negatively charged hydrocarbon ions would be formed. This difficulty can be overcome by assuming that the ethyl ion or radical, as it is disrupted from the crystal lattice, reacts in this condensed phase in a manner similar to the low temperature condensed phase reaction for tetramethyllead. It should give ethane and leave a carbonaceous residue, which would probably contain sodium carbide analogous to the formation of methane and carbon in our low temperature experiments. The small amount of other products formed by side reactions would not be detected by the method of analysis these authors used.

A striking contrast is shown between the thermal decomposition of tetraethylgermanium and that of ethylsodium. The former is a nonpolar substance that is easily vaporized. The metal atom is probably centrally located between the hydrocarbon groups and adjacent to the alpha carbon atoms. There is no possibility of a reaction similar to the major one which takes place in the decomposition of ethylsodium. The reaction is homogeneous in the gas phase. The chief products which Geddes and Mack[1] found were ethane, ethylene, hydrogen, methane, and higher olefins in amounts respectively of about 4, 2, 1, 1, and 1. These are not so greatly different from the products found in our high temperature reaction especially when it is taken into consideration that the ethyl radicals have the opportunity for a reaction which is denied the methyl radicals. That is, they can undergo disproportionation into the two stable products, ethane and ethylene.

Meinert[2] has recently studied the pyrolysis of tetraethyllead. In common with our results on the lower homolog, his results also point to two different reactions. One of these is a homogeneous reaction in the vapor phase. The other is a reaction in the condensed phase. His experiments on the decomposition of the liquid gave rise to the products which are analogous to the products we have postulated in our condensed phase reaction.

The Production of Isobutylene. Isobutylene is one of the lesser products formed in the thermal decomposition of tetramethyllead. Its amount, about 5%, is greatest at the lowest temperature used, where the wall reaction predominates, and decreases with a rise in temperature. Its presence might be

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[1] Loc. cit.

[2] R. N. Meinert: Paper presented before the Physical Chemical Division of the American Chemical Society at the Buffalo meeting, September, 1931.

overlooked were it not for the fact that in two independent cases isobutylene has been reported.   Hurd and Spence[1] reported small yields of it from the pyrolysis of n-butane and recently[2] considerably higher yields have been realized.   In the electrolysis of methylmagnesium bromide in ether solutions, Evans and Lee[3] found that isobutylene made up 10-17% of the anode gases when the concentration of the electrolyte varied from 1.45 to 1.09 molar. When the experiments with tetramethyllead, n-butane, and methylmagnesium bromide are compared, the only apparent point in common is that all may give a free methyl radical as a transient product.   Evidently, therefore, by some obscure mechanism, isobutylene is formed from it.

Summary

The thermal decomposition of tetramethyllead has been studied by the use of two different methods.   In one the substance was heated for a considerable time at normal pressures in sealed bulbs, whereas in the other it was heated at reduced pressures, using a flow method which gave an extremely short contact time.

The products of the reaction were identified.   The results indicate two sets of reactions, one taking place on the walls of the vessels and the other being a homogeneous gas phase reaction.   The low temperature reaction produced carbon and tarry substances and, curiously, also some isobutylene.

An attempt has been made to explain the mechanism of the formation of the products and also to correlate other experiments of a similar nature with this information.

Certain essential factors have been pointed out regarding the Paneth and Hofeditz experiment of removal of lead mirrors by free methyl radicals.

Evanston, Illinois.

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[1] Loc. cit.

[2] Hurd, Eilers and Pilgrim: unpublished data.

[3] Evans and Lee: Paper presented before the Physical Chemical Division of the American Chemical Society at the Buffalo meeting, September, 1931; F. H. Lee, Ph.D. dissertation, Northwestern University, 1931.

THE DISPERSION OF ALUMINA BY ACIDS*

BY HERBERT L. DAVIS

In the course of a current study of alumina lakes with acid dyes it became desirable to have more definite information as to the conditions under which alumina itself might be peptized by the common acids. The present paper demonstrates that with hydrochloric or acetic acids the effect of small additions is to disperse the alumina as a positively charged colloidal sol which may be precipitated by sodium sulphate. Sulphuric acid disperses alumina only slightly as the colloidal form and larger quantities are required, the systems as in the hydrochloric and acetic acids gradually becoming true solutions as the concentration of acid is increased. This study has shown that the reversible precipitation of alumina by heating is not merely a matter of heating increasing the hydrolysis of the aluminum acetate solution but requires some adsorbable electrolyte if the ageing of the alumina is not to result in an irreversible precipitation. Finally some comparison is made between the peptizing power of hydrochloric and sulphuric acids which should have some commercial significance.

The most interesting of the dispersing agents used is acetic acid and the description of the experiments with it will be given first. The alumina used was precipitated in the cold by the action of sodium carbonate on aluminum chloride, the alumina being washed on a Büchner funnel until it began to peptize slightly and visibly while there was still a slight test for chloride. It was then suspended in water so that the suspension contained 0.05 mol of Al_2O_3 per liter, ten cc portions of this well stirred suspension being taken for each system below, acetic acid added and the whole diluted to 20 cc. Systems were thus made up containing respectively 0, 0.4, 0.8, 1.2, 1.6, 2, 4, 6, 8, 12, 14, 16, 18, 20, 24, 32, 40, 80, 120, 160, 200, 240, 280, 320 mols of acetic acid per mol of alumina. The tube containing six mols of acetic acid per mol of alumina is equivalent to a 0.15 normal solution of neutral aluminum acetate.

At room temperature systems containing more than 40 mols of acetic acid cleared very quickly and within 1.5 hours the 6 mol system and beyond were completely dispersed. In fifteen hours 4 mols of acetic acid was able to give large dispersion to a slightly opalescent sol, while below that there was regular decrease in dispersion. The tubes were heated in a water bath and the 0.4 system appeared to be about 95% dispersed as compared with the tube containing no acid while the 0.8 tube and those above were completely cleared by thus heating. Of interest is the fact that altho tube 4 on first heating cleared completely, both it and tube 6 (the equivalent system) on further heating developed a very definite turbidity which did not settle out nor clear on

several weeks standing. This was confirmed on other systems and will be discussed later. The first result, then, of this run is that a mol of freshly precipitated and washed alumina can be dispersed into a perfectly clear sol by something less than 0.8 mol of acetic acid and that this represents about 13% of the six mols of acetic acid needed to form neutral aluminum acetate.

The dispersion of alumina has been studied by previous workers.[1] "H. Müller[2] boiled freshly precipitated hydrous alumina with 0.05 N HCl and found the amount of acid required for complete peptization to be one-seventy-second of that necessary to form $AlCl_3$; Pauli[3] used one-ninth of the theoretical amount and Kohlschütter[4] showed that the quantity of acid required was determined by the history of the sample. The dissolution of hydrous alumina in concentrated HCl is always preceded by sol formation; but H_2SO_4 does not form a sol." One of the important elements in the history of the alumina is the method of its preparation and it was observed that in certain of these systems the addition of the acetic acid had an immediate effect of liberating some gas from the alumina which was interpreted to be evidence that some of the carbonate used in precipitation was adsorbed on the alumina. This would have the effect of cutting down its peptization by acid.

The character of these dispersions was revealed by the addition of normal sodium sulphate solution to five cc portions of the systems. On the addition of one drop of sodium sulphate, system 4 (the tubes will be designated by the number of mols of acetic acid present per mol of alumina) and those below it coagulated rapidly and cold, and on heating to boiling precipitation was produced in all from 6 to 24 inclusive. With more acetic acid than this even four drops of sodium sulphate failed to give a precipitate either hot or cold. Those systems which required heat to bring about the flocculation of the alumina all cleared completely on cooling. With two drops of sodium sulphate some precipitation was produced in 6 and 8 which increased on heating and was permanent on cooling, the precipitation in 12 to 24 resulting only on heating and being reversible. With three drops of sodium sulphate the results are similar except that 12 and 14 are not completely reversible on cooling until they have stood for some time. With four drops of sodium sulphate the observations are the same, tube 8 being the last tube to give a permanent precipitate. This study shows that in the dispersion of alumina by acetic acid, those systems containing less than the equivalent amount of acid are easily and irreversibly coagulated by the addition of sodium sulphate. Systems containing an intermediate amount of acid are flocculated by the combined action of sodium sulphate and heat; and this flocculation is reversible on cooling, the reversibility increasing with the amount of acetic acid and decreasing with the amount of sodium sulphate used. Systems with more than 24 mols of acetic acid per mol of alumina are not flocculated under these conditions.

[1] Weiser: "The Hydrous Oxides," 115 (1926).
[2] Müller: Z. anorg. Chem., **57**, 311 (1908); cf. Schlumberger: Bull., (3) **13**, 60 (1895).
[3] Pauli: Kolloid-Z., **29**, 281 (1921).
[4] Kohlschütter: Z. Elektrochemie, **29**, 253 (1923).

The explanation of these facts is to be found in a consideration of the changes possible here. These are represented by the equations;

$$(Al_2O_3)_n + H^+ + Ac^- = (Al_2O_3)_n\ H^+ + Ac^- \tag{1}$$

$$Al_2O_3 + 6\ HAc = 2Al(Ac)_3 + 3H_2O. \tag{2}$$
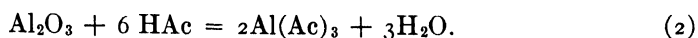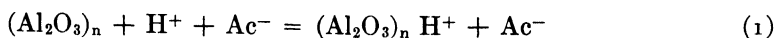
Equation 1 shows the peptization of the alumina by the adsorption of hydrogen ions to form a positively charged colloidal sol, while equation 2 shows the ordinary reaction to form the normal salt, aluminum acetate. The reverse of reaction 2 will of course be the hydrolysis of this salt. The production of a precipitate by the addition of sodium sulphate to such a system results from the adsorption of the strongly adsorbed negatively charged sulphate ion on the positively charged peptized alumina and thus serves as a proof of the existence of such colloidal alumina in the system. It is perfectly true that such addition of sulphate precipitating the colloidal alumina will tend to reverse the reaction shown by equation 2 so that a part of the aluminum may thus be precipitated which originally was present in true solution. But it is equally true that if all the aluminum be present in true solution none can be precipitated by the sodium sulphate. It appears highly probable that any such system contains some colloidal alumina which would be flocculated by a very strongly adsorbed negative ion. Thus for a similar series of tubes it was shown that, on heating, potassium ferrocyanide gave precipitation even in tubes containing as much as 420 mols of acetic per mol of alumina. This series was not investigated in as much detail as the sulphate series but it was observed that on adding one drop of the ferrocyanide there was no immediate effect; a slow clouding finally results in a precipitate in a system with 18 mols of acetic acid. This is quite analogous to the behavior of sodium sulphate containing 6 mols of acetic acid and therefore representing a far less stable system. A similar effect to the system containing the large amount of acetic acid was shown by adding two drops of the 0.5 M $K_4Fe(CN)_6$ to five cc of N $AlCl_3$. There was no immediate effect in the cold but the yellow solution gradually changed to a blue and finally a light blue precipitate settled out. On boiling a similar system there was an immediate deep blue precipitate which did not appear markedly different from ordinary flocculated alumina. The blue color is due to the oxidation of a part of the ferrocyanic acid produced. The most reasonable explanation of this phenomena is that there is here flocculation of alumina by a tremendously strongly adsorbed negative ion with a resultant hydrolysis of aluminum salt in solutions containing extremely small amounts of the alumina originally.

In the acetic acid systems it is obvious that the first dispersion is to a colloidal solution easily coagulated by sulphate. With increasing concentration of acetic acid the sol thus produced is more stable and resists such flocculation. Also increasing proportions of aluminum are present in true solution, the action of the acetic acid on the peptized alumina showing that the two reactions postulated above are actually consecutive and not mutually exclusive. Reaction 2 may be reversed by heating which usually increases

hydrolysis or by the addition of a strongly adsorbed negative ion capable of precipitating the alumina. Both these effects are opposed by the presence of excess acetic acid and this accounts for those systems in which no precipitate is observed.

The effect of ageing on alumina has been shown to be accompanied by a marked diminution in adsorbing power and in these systems too it has a similar effect. Alumina-acetic acid systems were made up as described above but from an alumina precipitated a month previously and during that time kept under water. It was washed so thoroughly that it settled extremely slowly in the stock bottle. The phenomena of dispersion were essentially those given above except that it required about 40 hours for the complete dispersion of the 6 system as compared with 1.5 hours for the fresh alumina. On adding sodium sulphate and heating there was precipitation in all systems to and including 32 mols of acetic as compared with 24 for the fresh alumina. The effect of ageing, then, is to increase the time necessary for dispersion and to decrease somewhat the stability of the sols thus produced.

A better idea of the effect of ageing may be obtained from some experiments made on a suspension of alumina prepared as above and permitted to stand for seven months. It was then found that the addition of an equal volume of normal acetic or hydrochloric acids did not produce peptization although this corresponded to twenty mols of acid per mol of alumina. The acetic acid tube was not distinguishable from a blank tube in which the sol was diluted with an equal volume of water. In the hydrochloric acid tube there was apparently a slight peptization of the surface layers of alumina which had been responsible for keeping the alumina somewhat dispersed for on standing most of the alumina in this tube settled out, leaving a clear supernatant liquid. The suspension was coagulated by sodium sulphate but much more slowly than a fresh alumina would have been. It is clear therefore that this alumina, containing practically no adsorbed salt, has aggregated a long way toward the insoluble state shown by alumina which has been heated to a high temperature. This loss in adsorptive power by purified alumina is of importance for such uses of alumina as lake making.

The Hot-Cold Reversibility

A very interesting phenomenon is the reversibility of the flocculation of the alumina from systems containing an excess of acetic acid and a small amount of the sodium sulphate. This was first reported by Gay-Lussac[1] who observed that a solution of aluminum acetate becomes turbid on heating and a large amount of alumina precipitates. If the solution is allowed to cool, the precipitate dissolves slowly and becomes transparent. On reheating and recooling, these changes may be repeated at will. With a dilute solution of aluminum acetate turbidity appears about 50° and a precipitate forms at a higher temperature. The precipitate must change gradually because it dissolves more slowly, when the solution is cooled, the longer the heating has

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[1] Gay-Lussac: Ann. Chim., **74**, 193 (1810).

lasted. With a more concentrated solution of aluminum acetate the temperature must be raised somewhat higher before turbidity occurs; but this solution also clears up when cooled.

"To determine the amount of alumina precipitated from an acetate solution by heating and the variation with the temperature, there were taken two equal portions of aluminum acetate made by mixing in the cold two solutions of alum and of lead acetate. One of these portions was raised to the boiling point and filtered at once, while the other portion was precipitated by ammonia. The two precipitates were washed and dried; after which it appeared that the first weighed about half as much as the second."

The data given above show the same phenomenon; but we are now ready to arrive at a more complete explanation than has previously been given. It is not alone a question of reversible hydrolysis but depends on a balance of forces, heat and sodium sulphate (or some other negative ion) tending to flocculate the alumina and the acid tending to disperse it. The aluminum acetate solutions heated by Gay-Lussac certainly contained sulphate from the alum either as the potassium sulphate or as lead sulphate which is several times as soluble as barium sulphate. With this in mind a solution of aluminum acetate was made by mixing cold aluminum sulphate and barium acetate solutions until there was no further precipitate with barium acetate and only a very slight slow turbidity with aluminum sulphate (a slight excess of barium acetate). This solution of aluminum acetate was made up to a normal concentration and diluted, tubes being heated quickly to boiling, stoppered, and set aside. Results are shown in Table I.

TABLE I

Effect of heating Aluminum Acetate Solutions

Concentration	Immediately	On standing four weeks
Normal	Turbidity	Settled out
0.7N 0.5N	Maximum turbidity	Settled out
0.25N	Less turbidity	No settling
0.15N	Faint turbidity	No settling
0.1N	Clear	Clear
0.05N	Clear	Clear

The aluminum acetate prepared by Gay-Lussac from the cold saturated solutions should have given him a solution about 0.7 N with respect to aluminum acetate. Such a solution of pure aluminum acetate does give a precipitate but in absence of sulphate and excess acetic acid the precipitation is irreversible. The faint permanent turbidity on heating the 0.15 N aluminum acetate thus made agrees exactly with that produced in the Al_2O_3-6 mols of acetic acid system previously mentioned. The irreversibility here is to be ascribed to an ageing agglomeration of the alumina at the boiling point and it is well known that such ageing is minimized by the presence of adsorbed

ions or molecules such as are present in the systems here prepared. In so far as the normal aluminum acetate gives a clear solution cold, the coagulation by increase of hydrolysis on heating should be reversed on cooling unless there be some irreversible change in the alumina, heating in closed tubes involving no loss of acid. The loss in ease of repeptization on cooling which was observed by Gay-Lussac is due to a gradual ageing on the repeated heating even in the presence of the salts.

In the experiments here recorded this reversibility is found only in the presence of excess of acetic acid and a small amount of sodium sulphate. It appears quite probable that the same phenomenon might be shown with other peptizing and precipitating ions for it appears to be due to a balance of forces. Thus the effect of heat and of sodium sulphate is to precipitate the aluminum while the acetic acid tends to disperse it. Thus it happens that in certain systems a small addition of sodium sulphate produces no precipitate until aided by the action of heat, such systems will clear on cooling since the presence of the electrolyte tends to minimize any irreversible change such as ageing on the part of the alumina. Increasing addition of acetic acid prevents this precipitation hot or cold, and systems which with sodium sulphate are coagulated cold will of course not redisperse on cooling after heating. It thus is probable that extremely small quantities of the sulphate would produce the reversible precipitation in the systems containing less than the equivalent amount of acid. This is what is involved in the discussion by Knecht.[1]

"Solutions of the normal acetate which contain other salts (like the alkaline sulphates or chlorides or alum) become turbid when heated, and form precipitates when boiled much more readily than the pure acetate; they dissociate, forming acetic acid in the free state, and precipitates of basic acetates, which redissolve on cooling, unless the acetic acid has been driven off by prolonged boiling. These results, which were obtained many years ago by Walter Crum, are not in harmony with the more recent researches of Liechti and Suida. The latter state that normal aluminum salts are not dissociated either by heating or by diluting with water.

"By adding to the solution of normal aluminum acetate the requisite amounts of sodium carbonate, solutions of basic acetates of varying basicity are obtained.

"The solutions of basic acetates are dissociated on heating; the more basic they are the lower is the temperature at which the dissociation begins; but the dissociation is retarded by dilution with water; in the absence of alkaline sulphates no dissociation is effected by dilution with water at the ordinary temperature. The precipitates formed by basic acetates in the absence of sulphates at higher temperature are not redissolved on cooling. They seem to consist chiefly of aluminum hydroxide.

"In the presence of alkaline sulphates—e.g., sodium sulphate—both the normal and the basic aluminum acetates are dissociated by diluting with water, and the dissociation by heat proceeds more readily than in the absence

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[1] Knecht, Rawson, and Loewenthal: "A Manual of Dyeing," 230 (1910).

of sulphates. The precipitates obtained by heating redissolve on cooling if formed in the presence of soluble sulphates."

"The commercial solutions of acetates and sulphate-acetates of aluminum are known in the trade as *red liquor*, because they are employed by cotton dyers and calico printers as mordants for alizarin reds. The composition of the red liquors varies greatly, and their value for different styles of work is better determined by practical tests than by analysis. They are prepared by the double decomposition of normal aluminum sulphate and commercial acetate or pyrolignite of lime, with or without addition of chalk or soda, and always have a yellowish-brown appearance from the presence of empyreumatic substances."

Several experiments have confirmed the first finding that a solution of aluminum acetate containing very slight excesses of either of the salts used to prepare it is partially and irreversibly precipitated on heating. But a solution of acetate containing a definite excess of aluminum sulphate is very readily reversible, producing a heavy precipitate of alumina on boiling and clearing completely on cooling. In aluminum sulphate we have at the same time a very effective peptizing agent for alumina, the aluminum ion, and a very effective coagulant, the sulphate ion. Both opposing forces being present in the same salt, the action of temperature decides which shall be most effective and the high adsorption of the salt prevents the irreversible ageing of the alumina precipitated by the heat and thus provides for the reversibility observed.

Dispersion of Alumina by Hydrochloric Acid

The procedure of the acetic acid dispersion was repeated eight days later with the same alumina and hydrochloric acid solutions, systems were made up with 0, 0.4, 0.8, 1.2, 1.6, 2, 4, 6, 8, 12, 14, 16 mols of acetic acid per mol of alumina. The course of the dispersion was essentially the same as in the acetic acid series, the greater dissociation of the acid making up for the greater age of the alumina. Over night two mols of acid gave complete dispersion and the next day the first eight tubes of the set were put in the water bath, boiling for one hour. Tube 0.8 and above were completely clear and tube 0.4 appeared about 98% peptized—slightly more completely than the comparable acetic tube.

Addition of one drop of normal sodium sulphate to five cc portions of these systems gave precipitation in the systems 2 and below, but not in 4 or above cold or hot. When five cc of saturated sodium sulphate was added to five cc of the 4 system there resulted a precipitate on heating which cleared on cooling. The system 6 containing normal aluminum chloride gave no precipitate even with saturated sodium sulphate cold or hot. It is clear again that small amounts of hydrochloric acid also peptize the alumina to form a sol whose stability increases with acid concentration and finally passes over to true solution.

The peptization by hydrochloric acid is shown to be not very different from that by acetic acid, 0.4 mol of either acid per mol of alumina giving nearly complete peptization to a clear sol. This is interesting as pointing to

two possible explanations, neither of which have been fully evaluated before. One of the explanations is that peptization of the alumina results not only from the adsorption of the hydrogen ion but also from the adsorption of the acetic acid molecule. The 0.4 mol systems have sufficient acid so that alone it would be 0.02 N and the data of Kendall[1] demonstrate that such a concentration of acetic acid is about three per cent dissociated whereas of course the hydrochloric acid is completely dissociated. There surely is not thirty times the peptization in the hydrochloric acid systems as there should be if hydrogen ion concentration alone is the important factor.

This is demonstrated also by the quantitative measurements of Weiser[2] in which he added five and ten cc of 0.2 N acids to 150 cc of an alumina suspension containing 0.750 g. alumina. After suitable treatment the systems were filtered and the unpeptized alumina weighed.

TABLE II

Weiser's Peptization of Alumina by Acids

	Total Peptized	By Acid		Total Peptized	By Acid
None	0.477 g.		None	0.454	
5 cc Acetic	0.508	0.031	10 cc Acetic	0.543	0.089
5 cc HCl	0.580	0.103	10 cc HCl	0.653	0.199

With five cc of 0.2 N acetic acid in 155 cc its dissociation is given as about 5.2% or only about one-nineteenth that of the hydrochloric acid and yet the peptizing effect due to the acetic is nearly one-third that of the hydrochloric acid. With 10 cc of acetic acid in 160 cc the dissociation is 3.8% so that the dissociation of the hydrochloric acid is about 26 times that of the acetic acid and yet the peptization by the stronger acid is only a little more than double that brought about by the weak acid.

Concerning this experiment Weiser[3] says later: "If we assume as Lotter-moser does, that a peptizer must contain one of the ions of the disperse phase, then the first step in the peptization of alumina by an acid or salt would be interaction with the formation of some aluminum ion. This would seem to be an unnecessary step in view of the stronger peptizing action of hydrogen ion than of aluminum ion. On account of the relatively small ionization of acetic acid, its peptizing power is less than that of HCl or HNO_3."

In view of these facts it appears that we may have peptization of the alumina by the acetic acid molecules. This would not be a new or unusual phenomenon for of course many examples of peptization by the adsorption of a molecule are recorded and Weiser says, p. 120; "A sol results by precipitation (of alumina) in the presence of glucose. In some preliminary experiments on grinding alumina in a colloid mill with glucose, Utzino[4] claimed to get a sol, the maximum stability of which does not occur with the finest state of subdivision. These observations should be repeated." The peptization of casein by acetic acid appears to be due largely to the undissociated acid.

[1] Kendall: J. Chem. Soc., 101, 1280 (1912).
[2] Weiser: J. Phys. Chem., 24, 521 (1920).
[3] Weiser: "The Hydrous Oxides," 115 (1926).
[4] Utzino: Kolloid-Z., 32, 149 (1923).

But peptization by the undissociated acetic acid is not the only way it is possible to explain these facts. It is suggested that the action of alumina in adsorbing hydrogen ions from an acetic acid solution may not be markedly dissimilar from a neutralization of the acid by alkali, both removing hydrogen ions and permitting the dissociation to proceed further to a new equilibrium. To take a somewhat extreme case it is known that if a sol of alumina is coagulated by the required amount of a ferrocyanide and a small amount of ferric salt is added, no Prussian blue is formed until after an appreciable interval of time. A comparable removal of hydrogen ion from the acetic acid solution would cause a further dissociation of the acetic acid to restore the equilibrium. A way suggests itself for deciding whether the unexpectedly large effectiveness of acetic acid in peptizing alumina is due to adsorption of the molecule or to this pseudo-neutralization of the acetic acid with the consequent increased dissociation.

This dissociation of the acetic acid should be repressed greatly by the addition of potassium acetate and if the peptization of the alumina were due to adsorption of hydrogen ions, this peptization should be diminished by the salt addition. If, however, molecules of acetic acid are responsible, salt addition should have little effect. To answer this question, two series of systems were made up, one containing 0.4, 0.5, 0.6, 0.7, 0.8 mols of acetic acid per mol of alumina, and the other the same amount of acetic acid plus an equivalent amount of potassium acetate. All these and a blank in which the alumina suspension was diluted with water only were heated in a water bath for a half hour. With acetic acid alone tubes 0.8 and 0.7 were completely clear; below 0.6 an increasing turbidity appeared until 0.4 was again about 95% dispersed as compared with the blank. The comparable tubes containing potassium acetate were none of them nearly clear although all showed considerable dispersion. The 0.8 system with the salt was about three times as turbid as the 0.4 system without the salt. It is clear, then, that potassium acetate by repressing the ionization of the acetic acid decreases its peptizing power very remarkably. In the absence of the alumina the dissociation of the acid would be very slight but the dispersion of the alumina observed shows that in presence of alumina, the salt is not able completely to repress the dissociation of the acid. This does not rule out some peptization of the alumina by acetic acid molecules but does establish that an important factor is the additional dissociation of the acetic acid to restore equilibrium in the presence of alumina.

There still remained the possibility that the decrease just reported was due to a coagulating action on the part of the acetate ion whose concentration is doubled by the salt addition. In order to meet this possible objection and to get an idea of the relative importance of the two effects, a series of systems was made up containing 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 mols of hydrochloric acid per mol of alumina, and another series containing the same amounts of hydrochloric acid plus equivalent amounts of acetic acid. If the peptization be one due solely to hydrogen ion adsorption, addition of acetic acid which in the

hydrochloric acid solution would practically be non-ionized would not increase the dispersion in the mixed systems. If, however, the dispersion in the mixed series proves greater than in the presence of hydrochloric acid alone, the conclusion in this case is that the molecular acetic acid has peptizing power. This was actually found to be the case for all the mixed systems were much more dispersed than the corresponding systems with only hydrochloric acid and therefore acetic acid does peptize even in hydrochloric acid solutions. A rough measure of the effect is seen in the observation that the system containing 0.3 mol HCl + 0.3 mol acetic acid per mol of alumina was of about the same low turbidity as the system with 0.5 mol HCl. This means that the molecule of acetic acid is about two thirds as effective as hydrogen ion if the hydrochloric acid is here able completely to repress the dissociation of the weaker acid in presence of alumina. In view of the fact that practically all the hydrochloric acid is probably adsorbed on the alumina, this may be open to question, but the conclusion is inevitable that molecular acetic acid does peptize alumina under these conditions and that the large effectiveness of acetic acid is due both to this cause and to the increased dissociation in presence of the alumina. The tubes made for these experiments confirm earlier runs as to the essential equality of these acids, 0.6 mol HCl or 0.7 mol acetic acid per mol of alumina being the minimum amounts giving clear sols.

The Dispersion of Alumina by Sulphuric Acid

At the same time and with the same alumina as that used for the HCl experiments a similar series was prepared containing; 0. 0.4, 0.8, 1.2, 1.6, 2, 2.4, 2.8, 3.2, 3.6, 4.0, 4.4, 4.8, 5.2, 5.6, 6, 8, 12, 16 equivalents (not mols) of sulphuric acid per mol of alumina. Again system 6 containing six equivalents of sulphuric acid per mol of alumina represents a 0.15 N solution of normal aluminum sulphate. Over night at room temperature system 5.6 and above cleared completely, all the rest having precipitate, tubes 3.2 and above having clear supernatant liquids while those below showed turbidity except for 0.8 which was quite clear. On longer standing, tubes 4.8 and 5.2 cleared except for a definite persistent turbidity. Heating for a half hour in a boiling bath produced no essential change aside from a general agglomeration of the precipitates.

Again normal sodium sulphate was added to five cc portion of the supernatant liquids. In the cold one drop of the sodium sulphate produced no immediate turbidity in any tube but on heating to boiling tubes 0.8 to 4.4 all gave definite turbidity while those above remained clear. Of these 0.4 and 0.8 cleared on standing, while the rest were permanent overnight. Increasing sodium sulphate gave increasing turbidity which also increased in the series of 1.6 to 4.4 but even 2 cc of saturated sodium sulphate gave no precipitate in tubes 4.8 and above. It was also observed that adding 2 cc of saturated sodium sulphate solution produced a precipitate in 4 and 4.4 which redissolved on cooling. This hot-cold reversibility, then, is shown in low acid systems with small addition of salt and in higher acid systems with addition of saturated salt solution. This again supports the balance of forces explanation previously advanced.

The study of this system is somewhat more complicated than those which have preceded it and this is chiefly by reason of the stepwise dissociation of the sulphuric acid. In the most dilute (0.4) solution there is competition between the hydrogen ion and the sulphate ion with the result that this system shows only slight settling as compared with the blank. In the 0.8 system the adsorption of the sulphate goes up more rapidly than that of the hydrogen ion and complete settling of visible particles takes place and nearly complete as far as the addition of sodium sulphate is concerned. In the more acid solutions the strongly adsorbed sulphate ion is increasingly locked up in the less strongly adsorbed acid sulphate ion which is less and less able to prevent the peptizing action of the hydrogen ion. This results in practically complete dispersion on adding 5.2 equivalents of sulphuric acid per mol of alumina.

In view of the turbidities and precipitates produced in these intermediate systems by the addition of sodium sulphate to the supernatant liquids the question is raised as to whether sulphuric acid too may not peptize alumina before carrying it into true solution. The phenomena are not essentially different from those observed in the acetic acid and hydrochloric series and the same explanation should apply.

The Relative Dispersing Power of Sulphuric and Hydrochloric Acids on Alumina

One of the important industries employing alumina is the lake industry in which alumina is treated with a dye to form a colored lake to serve as the pigment in paints, inks, etc. The usual method is to precipitate the alumina from aluminum sulphate by means of sodium carbonate or some other suitable alkali, wash the alumina several times by decantation and then add the dye solution with such salts as may assist dye adsorption or modify the color properly. It is obvious that several steps, much time and material and trouble would be saved the lake maker and the manufacturing chemist supplying the aluminum sulphate if this process could be interrupted just before the sulphuric acid is added to the bauxite (refined) to make the aluminum sulphate. This alumina could be supplied directly to the lake maker and by the addition of a small amount preferably of hydrochloric acid peptized to a clear, positively charged, colloidal sol. By the addition of the solution of the sodium salt of the acid dye, the strong adsorption of the acid dye anion would neutralize the positive charge on the alumina and precipitate it as a lake which should be more satisfactory than those made by the standard procedure.

The bauxite may be peptized to any desired degree by increasing addition of acid and altho it may not have nearly so high an adsorptive capacity as the freshly precipitated hydrous alumina, it may very well be quite comparable to such an alumina after it has been aged during the process of washing. It appears highly probable that it will have sufficient capacity to adsorb any required commercial amount of dye.

The question arises then: If one wished to disperse alumina with the minimum amount of acid, which acid should be chosen? The data given above furnish an answer to this question. Under the conditions a clear dispersion

of a mol of alumina requires o.8 mol of hydrochloric acid or 5.6 equivalents of sulphuric acid, o.4 mols of HCl or 4.8 equivalents of sulphuric acid giving systems of the order of 95% dispersed. Taking the figures for the clear systems, and the equivalent weight of sulphuric acid as 49, this means that 36.5 g. of HCl will have as much dispersing power as $7 \times 49 = 343$ g. of sulphuric acid, or nearly ten times as much.

These data are however for hydrous alumina and we know that a commercial material even partly dried will require different amounts of acid. Alumina calcined above 1000° loses nearly all its solubility in acids and we should expect all gradations between that and the fresh hydrous alumina. In order to get some idea of what might be expected of a refined commercial bauxite, a sample of alumina was precipitated, washed and dried in an oven at 108° for fifteen hours when it had approximately the composition $Al_2O_3.3H_2O$. To portions of this dried alumina various amounts of hydrochloric and of sulphuric acid were added in a constant volume. Heating for fifteen hours at 90° produced no change further than those observed in one hour. These indicated that for such an alumina four mols of HCl or 12 equivalents of sulphuric acid are required to disperse a mol of alumina. This means that 36.5 g. HCl are equivalent to $3 \times 49 = 147$ g. H_2SO_4 in this dispersion.

Conclusions

1. The action of acetic, hydrochloric, and sulphuric acids on freshly precipitated and washed alumina has been observed and it is shown that, under the conditions employed, complete dispersion of a mol of alumina is achieved by the use of o.8 mol of the first two acids while 5.6 equivalents of sulphuric acid were required.

2. In all three acids a part of the alumina is present as a positively charged colloidal sol capable of being precipitated by the addition of sodium sulphate; this is least with sulphuric acid.

3. In all three cases certain intermediate concentrations of acid are shown to give with sodium sulphate a precipitate only on heating. In most of such instances these precipitates redissolve on cooling and it has been shown that this reversibility is a result of an approximate balance between the coagulative effects of heat and the sulphate ion and the peptizing effect of the hydrogen ion. Pure aluminum acetate coagulates partially and irreversibly on heating unless there be present some electrolyte to prevent the irreversible ageing of the alumina.

4. It is shown that freshly precipitated alumina requires about ten times the weight of H_2SO_4 as of HCl to give a clear dispersion, while with dried alumina comparable to a bauxite, more of either acid is required and the ratio is about four.

5. A comparison of the peptizing power shows that acetic acid is far more effective, as compared with hydrochloric acid, than it should be on the basis of ionization alone. This is due both to peptization of alumina by acetic acid molecules and to an increased dissociation of the acid as alumina adsorbs hydrogen ions.

Cornell University.

THE REACTION BETWEEN BARIUM SULPHATE AND ALUMINA AT HIGH TEMPERATURES*

BY HAROLD SIMMONS BOOTH AND ROLAND WARD**

All barium salts of commercial importance are easily obtained from barium carbonate. Unfortunately the most plentiful barium mineral is barytes. The methods hitherto used for the manufacture of barium compounds from barytes depend upon its reduction with carbon to give the water-soluble sulphide, sulphite, thiosulphate, etc. From an aqueous solution of these, the preparation of pure barium products, either by crystallization or precipitation, leads to a product contaminated with sulphur compounds. Hence it seemed advisable to investigate the production of water-soluble compounds of barium from barytes by methods yielding a sulphur-free product.

Historical

When an alkali or alkaline-earth sulphate is heated with certain refractory oxides, SO_3, SO_2 and O_2 are evolved leaving a residue partially soluble in water. The decomposition of barium sulphate has been accomplished by this method using silica, alumina, magnesium oxide and barium oxide.

1. *Reaction with Silica.*

Mosttowitsch[1] states that when barium sulphate is heated alone its dissociation becomes appreciable at 1500°C. while in presence of silica decomposition begins at 1000°C. Mlle. G. Marchal[2] gives the dissociation pressure of $BaSO_4$ at 1800°C. as 10 mm. while a mixture of $BaSO_4$ and SiO_2 has the same dissociation pressure at 1250°C. P. P. Bundikov and E. A. Shilov[3] report that $BaSO_4$, when heated with silica in an electric furnace at 1000°C. decomposes to the extent of 97.7%. Two silicates,[4] $BaSiO_3$ and Ba_2SiO_4 are known and the latter, on repeated extraction with water leaves a residue which approaches the composition of the former, the solubility of which is given by Jordis and Kanter as about 1.28 g. per liter. According to Bundikov and Shilov the reaction product at 1000°C. is $BaSiO_3$. No information regarding the reaction product at higher temperatures is available.

[1] Metallurgie, **6**, 540-67; Chem. Abst., **5**, 841 (1911).

[2] Bull., **39**, 40-8 (1926).

[3] J. Soc. Chem. Ind., **42**, 297-9 (1923).

[4] H. LeChatelier; Ann. mines, **1887**, 345-404; E. Jordis and E. H. Kanter: J. Chem. Soc., **54**, ii, 1021 (1888).

2. *Reaction with Alumina.*

M. G. Arth[1] reported some reactions of aqueous solutions of barium aluminate which was supplied to him by M. Asselin who prepared it by heating barium sulphate and bauxite at high temperatures.

Gaudin[2] (1862), Martin[3] (1915), and Hershman[4] (1917) have observed the formation of an aluminate of barium when a mixture of barium sulphate, alumina and carbon is heated over 1000°C.

Hershman (loc. cit.) claims that barium aluminate is produced by heating $BaSO_4$ and Al_2O_3 in equimolecular proportions with an excess of lime and that the reaction may be assisted by steam.

In a patent[5] granted to G. W. Morey, it is stated that to produce tri-barium aluminate ($3BaO.Al_2O_3$) containing some free BaO, barium sulphate (3 mols) is heated to 1150°C. to 1400°C. with alumina (1 mol.).

Mlle. G. Marchal found that the decomposition of barium sulphate with alumina proceeds at 1200°C. to 1300°C. to a greater extent than with silica or kaolin. There are also some conflicting statements regarding the nature of the product of this reaction. Morey (loc. cit.) claims that tri-barium aluminate is produced at 1150°C. to 1400°C. while E. Martin[6] finds that tri-barium aluminate is only formed above 1500°C. M. G. Arth (loc. cit.) found that the solution obtained by extraction of Asselin's product with water, contained 12.6 gm. Al_2O_3 and 23.3 gm. BaO per liter. The mol. ratio Al_2O_3/BaO was 0.811. Upon standing in an open flask a deposit of Al_2O_3 and barium carbonate was obtained and the ratio of Al_2O_3 to BaO in the solution became 0.817. Analysis of commercial barium aluminates by A. J. J. Vandervilde[7] shows compositions ranging from 5 Al_2O_3.3BaO to 10 Al_2O_3.7BaO. Tammann and Pape[8] seem to be of the opinion that the mono-barium aluminate is produced up to 1360°C. E. Martin (loc. cit.) reported that repeated extraction of barium aluminate with water yields solutions increasingly richer in barium and residues correspondingly richer in alumina. He reports compounds of the general formula, $n Al_2O_3.(n + 1)BaO$. The final product is $Al_2O_3.2BaO$. Tri-barium aluminate, according to Martin, forms much more stable solutions.

3. *Reactions with Other Oxides.*

S. B. Newberry and H. N. Barret[9] patented a process for the production of barium oxide by heating barium sulphate to 1500°C. with magnesium oxide. They also claim that a finely divided mixture of barium oxide and barium sulphate when heated to 1460°C. evolves sulphur dioxide and oxygen leaving pure barium oxide.

[1] Bull., (3) **27**, 293-302 (1902).
[2] Gaudin: Compt. rend., **54**, 687 (1862).
[3] E. Martin: Monatschifti Sci., (5) **5**, 228-32 (1915).
[4] Hershman: U. S. 1240651, Sept. 18 (1917).
[5] U. S. 1688084, Oct. 16 (1928).
[6] Chimie et Industrie, **23**, 564-572 (1930).
[7] Bull. soc. chim. Belg., **26**, 319-20 (1912).
[8] Z. anorg. Chem., **127**, 43-68 (1923).
[9] U. S. 133392, March 30, 1915.

It is evident from the foregoing summary that the reaction between barium sulphate and alumina holds the greatest practical possibilities both on account of the temperature range and the solubility of the product. The conflicting nature of the data also warrants a more thorough investigation of the reaction. This paper deals with the reaction of barytes with bauxite at temperatures between 1100°C. and 1450°C. using mixtures of composition varying from excess of barytes to excess of bauxite.

Experimental

A. *Preparation of Mixtures.*

The crushed barytes rock was powdered in a ball-mill until 90% passed through a 200 mesh screen. Analysis of the powder showed the following composition:

	Per cent
$BaSO_4$ from hydrochloric acid extract	2.90
$BaSO_4$ residual	93.51
Fe_2O_3	1.09
Al_2O_3	0.34
Silica	1.43
	99.33

The bauxite was powdered to the same fineness as the barytes. Analysis of the powder gave the following composition:

Al_2O_3	62.91
Fe_2O_3	1.00
Silica	6.33
Volatile material by difference	29.76
	100.00

The requisite amounts of barytes and bauxite were weighed out, mixed by quartering and finally ground in a ball mill for twelve hours. Intimate and uniform mixtures were obtained by this method. The following mixtures were prepared.

Number	1	2	3	4	5	6	7
Parts bauxite to 100 pts. barytes	14.63	29.26	43.89	87.78	131.67	175.56	75.61

An attempt was made to prepare mixtures of pure $BaSO_4$ and alumina by making a suspension of precipitated $BaSO_4$ in aluminum sulphate solution and precipitating the alumina by addition of ammonia. The mixtures so prepared were found to be unsatisfactory.

In all experiments the mixtures were heated in covered platinum crucibles in a Globar electric furnace[1] the temperature measurements being made with an optical pyrometer of the disappearing filament type. The readings were re-

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[1] Booth and Ward: Ind. Eng. Chem., Anal. Ed., April 15 (1932).

producible to about ± 5 centigrade degrees, and the furnace temperature could be controlled within the same range. For comparison of the extent of reaction in different mixtures the crucibles were either placed in the cold furnace, heated to the desired temperature for a certain time and allowed to cool in the furnace or they were introduced into the furnace at the required temperature and withdrawn after specified time interval. To determine the reaction velocities the latter procedure was used. The method of heating was found to have considerable influence on the results. The samples from the furnace were ground in an agate mortar, placed in weighing bottles and kept in a desiccator over BaO[1] until required for analysis.

The course of the reaction was followed by analysis. When bauxite has been heated for a short time over 1000°C. its solubility in hot dilute hydrochloric acid becomes negligible, while barium aluminate is easily dissolved. The mixtures were extracted with hot dilute hydrochloric acid filtered and washed by decantation till free from chloride. The barium in the filtrate was

TABLE I

Typical Analysis of Furnace Product

Number	1	2
Mass of sample from furnace 1	1.0572	1.2366
Mass of $BaSO_4$	0.1482	0.1724
Filtrate Mass of Al_2O_3	0.0723	0.0729
Mass of Fe_2O_3	0.0025	0.0031
Mass of SiO_2	0.0218	0.0268
Total mass from filtrate	0.2448	0.2812
Mass of $BaSO_4$	0.5890	0.6964
Residue Mass of Al_2O_3	0.3012	0.3467
Mass of Fe_2O_3	0.0108	0.0133
Mass of SiO_2	0.0320	0.0396
Total mass of residue should be (A)	0.9330	1.0960
Mass of dry undecomposed mixture	1.1778	1.3772
Mass extracted 11.	0.1939	0.2220
Mass of residue 1 − 11 = B	0.8633	1.0146
Mass of residue if $BaSO_4$ were completely decomposed (C)	0.7308	0.8568
A − B	0.0697	0.0814
A − C	0.2022	0.2392
Fraction of $BaSO_4$ in residue decomposed	0.3446	0.3402
%$BaSO_4$ decomposed in residue	27.54	27.27
%$BaSO_4$ extracted	20.10	19.84
Total % decomposition	47.64	47.11
Molecular ratio Al_2O_3/BaO in extract	1.114	1.046
Molecular ratio $Al_2O_3/Ba(AlO_2)_2$ in residue	2.392	2.343
Molecular ratio $Al_2O_3/Ba(AlO_2)_2$ in extract	0.114	0.045

[1] Booth and McIntyre: Ind. Eng. Chem., Anal. Ed., **2**, 12 (1930), have shown that BaO is an excellent desiccant.

determined as $BaSO_4$ and the aluminum as Al_2O_3. For temperatures below 1260°C. this procedure was found to be satisfactory but for higher temperatures it was necessary to make a complete analysis since not all of the barium sulphate which had been decomposed could be extracted with acid. A typical complete analysis is given in Table I.

TABLE II

Barytes-Bauxite Mixtures

Mixture	Temperature °C.	% $BaSO_4$ decomposed	Mol Ratio Al_2O_3/BaO in HCl aq. extract
1	1100	3.01	1.57
2	1100	3.63	1.86
3	1100	4.90	1.734
4	1100	9.35	1.788
5	1100	13.29	1.734
6	1100	12.10	1.702
3	1260	14.24	2.076
4	1260	20.21	2.182
5	1260	27.28	1.676
6	1260	30.55	1.210
3	1290	10.92	1.737
4	1290	13.63	1.834
5	1290	18.37	1.659
6	1290	25.14	1.555

TABLE III

Barytes-Bauxite Mixture No. 5

Time of heating (t) minutes	log t.	Temp. °C.	% decomposition of $BaSO_4$ on basis HCl soluble	Mol ratio Al_2O_3/BaO in HCl aq. extract
15	1.1761	1182	9.31	1.022
30	1.4771	"	11.90	1.013
60	1.7782	"	13.29	1.367
90	1.9542	"	13.87	1.367
120	2.0792	"	14.49	1.329
150	2.1716	"	15.30	1.293
210	2.3222	"	15.85	1.265
270	2.4314	"	16.66	1.402
15	1.1761	1238	12.37	1.169
30	1.4771	"	12.87	1.108
60	1.7782	"	15.29	1.218
90	1.9542	"	16.32	1.153
120	2.0792	"	16.99	1.274
150	2.1761	"	17.27	1.198
180	2.2553	"	17.65	1.165
240	2.3802	"	18.10	1.523

TABLE IV

Barytes-Bauxite Mixture No. 5

Time in heating (t) minutes	log t.	Temp. °C.	% Barium dissolved in HCl aq.	% Barium total decomposed	Mol ratio Al_2O_3/BaO in HCl aq. extract
90	1.9542	1340	27.64	65.12	1.122
150	2.1761	''	36.44	75.98	1.127
270	2.4314	''	44.17	82.31	1.194
30	1.4771	1390	20.15	50.61	1.586
90	1.9542	''	59.71	85.72	1.322
150	2.1716	''	77.85	98.20	1.243
210	2.3222	''	77.43	99.39	1.175
60	1.7782	1440	66.01		1.054
120	2.0792	''	82.57		1.215
240	2.3802	''	82.47		1.082

TABLE V

Barytes-Bauxite Mixtures Nos. 3, 4, 5, and 6 at 1370°C.

Mixture	Time of heating (t) minutes	log. t	% Barium dissolved by HCl aq.	% Barium total decomposed	Mol ratio Al_2O_3/BaO in HCl aq. extract
3	60	1.7782	22.02	42.32	1.209
	120	2.0792	36.72	44.45	1.030
	180	2.2553	48.90	48.90	1.076
	240	2.3802	60.30	60.30	1.077
	420	2.6232	69.34	69.34	.950
4	60	1.7782	30.42	53.56	1.183
	120	2.0792	51.44	74.73	1.071
	180	2.2553	62.38		1.085
	240	2.3802	77.29		1.077
5	60	1.7782	35.11	75.23	1.223
	120	2.0792	40.36	81.79	1.026
	180	2.2553	58.69		1.129
	240	2.3802	75.34		1.077
6	60	1.7782	36.56	65.29	1.170
	120	2.0792	54.34		1.108
	180	2.2553	67.30		1.097
	420	2.6232	55.59	100.0	1.127

TABLE VI

Barytes-Bauxite Mixture No. 7 at 1390°C.

Time of heating (t) minutes	log t	% Barium		Mol ratio Al₂O₃/BaO in HCl aq. extract
		dissolved by HCl aq.	total decomposed	
60	1.7782	19.92	47.38	1.080
120	2.0792	44.01	66.30	1.049
180	2.2553	61.85	79.10	1.023
240	2.3802	82.68	97.17	.999
420	2.6232	93.05	100.	1.000
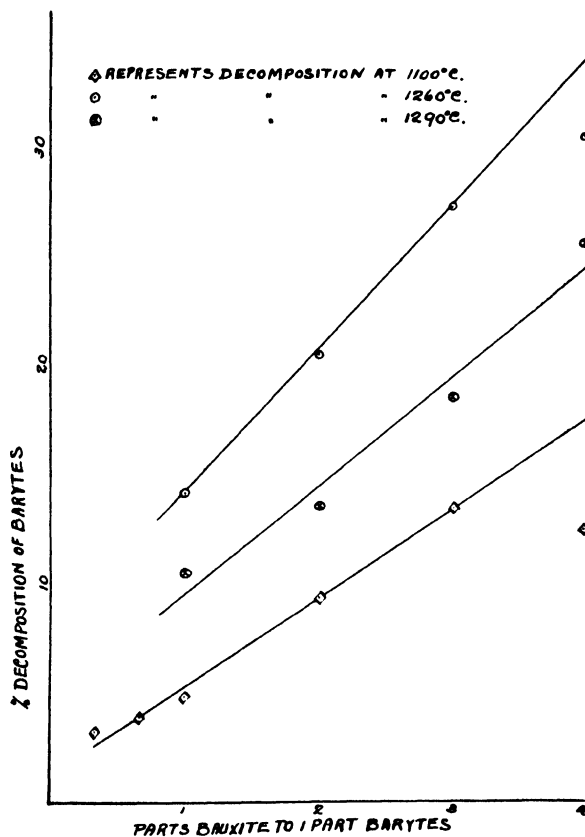
FIG. 1

Results

Table II gives the results of experiments on mixtures 1 to 6. For the two temperatures 1100°C. and 1260°C. the mixtures were heated slowly to the reaction temperature, maintained at that temperature for 1½ hours and allowed to cool in the furnace. This was repeated three times. In the experiment at 1290°C., however, the heating was not interrupted and the time of heating was only three hours. The results are shown graphically in Fig. 1. Tables

III–VI give the results of experiments on reaction velocity in mixtures 3 to 7 at various temperatures. In all cases the mixtures were placed in the furnace at reaction temperature and withdrawn after the time interval given in column 1. Table III refers to reaction in mixture 5 at 1182°C. and 1238°C. In these the analysis consisted of the determination of the percentage of barium which
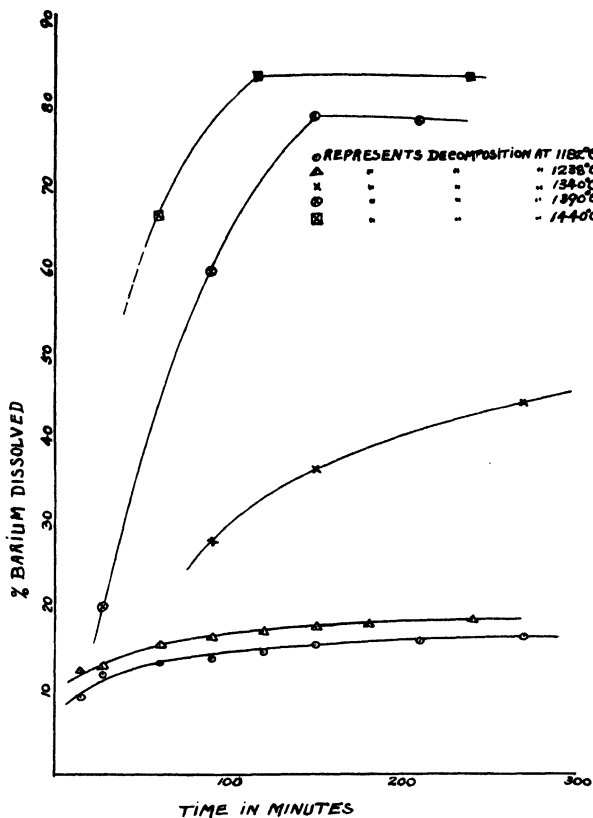
FIG. 2

Time-decomposition curves for mixture 5 on basis of HCl aq. solubility

could be extracted with dilute hydrochloric acid. For higher temperatures a complete analysis was made. The last column in all the tables gives the molecular ratio Al_2O_3/BaO in the extract.

Discussion of Results

The reproduction of results at temperatures below 1250°C. is fairly easy. Above this temperature, however, a slight temperature difference over a long period of time can have an appreciable effect upon the amount of decomposition. It was found that after the heating elements had been used for some time, their emissivity for visible light increased. This caused more reflection from the furnace walls and resulted in a higher temperature reading on the optical pyrometer. In order to have reproducible temperature conditions,

the heating elements must be new. For each time-decomposition curve the same heating elements were used throughout. From Fig. 2 it can be seen that at temperatures above 1350°C. the initial part of the reaction becomes very rapid. Since it takes the crucibles several minutes to come to the furnace temperature, experiments of 30 minutes duration and less are likely to be quite inaccurate.

Table I gives an analysis in duplicate of a partially decomposed mixture. The agreement is close enough for practical purposes. The percentage of barium extracted can be duplicated within 0.5% but for the total decomposition the results are likely to be quite erratic. The source of the trouble is in the analysis of the residue, particularly in the removal of the alumina by fusion with potassium bisulphate. In mixtures of high alumina content this is exceedingly difficult. In these cases where the results were at considerable variance, they were omitted from the tables.

Conclusions

Examination of Table II shows that at 1100°C. the percentage decomposition of the barium sulphate is very low. The curves in Fig. 1, however, show that the decomposition increases with the proportion of alumina in the mixture at the lower temperatures up to Mixture 5. At 1290°C. the decomposition increases linearly up to Mixture 6; but in this case the mixtures were heated continuously while at the lower temperatures the heating was interrupted.

That the method of heating the mixtures has some influence on the decomposition was demonstrated by a later experiment when Mixture 5 was heated slowly up to 1390°C. and maintained at that temperature for an hour; the total time of heating was four hours. The percentage of barium rendered acid-soluble was 23.18 compared with 43 in the case of the mixture which was placed in the hot furnace (at 1390°C.) and removed after one hour.

In column 4 of Tables II and III it is shown definitely that, at 1000°C. to 1290°C. the molecular ratio of Al_2O_3/BaO in the extract is considerably greater than unity in all cases. From this it may be safely deduced that there is no tri-barium aluminate present in the reaction product obtained by heating the mixtures for three or four hours at 1000°C. to 1290°C. The presence of an excess of barium sulphate in the mixture does not change the ratio appreciably.

There is no evidence here of catalytic action.

The time-decomposition curves for Mixtures in Figs. 2 and 3 are plotted from the data of Tables III and IV. They present some interesting features and reveal some facts which are of practical value.

Mlle. Marchal (loc. cit.) suggested that the increased decomposition of sulphates, when heated with silica and alumina, was due to the heat of formation of silicates and aluminates which lowered the temperature of dissociation. This means, of course, that there would be local heating; the molecules of sulphate near the reaction zone would be heated above their dissociation

temperature; and the free oxide would be produced. Tables III and IV show that after fifteen minutes at 1182°C. and 1238°C. there is no free barium oxide in the soluble product. If the heat liberated in the reaction does cause the production of free barium oxide, diffusion of the latter through the reaction product and its subsequent reaction with the alumina must occur immediately. The phenomenon, if it occurs at all, must be of short duration.

△ REPRESENTS DECOMPOSITION AT 1340°.
○   "   "   " 1390°.
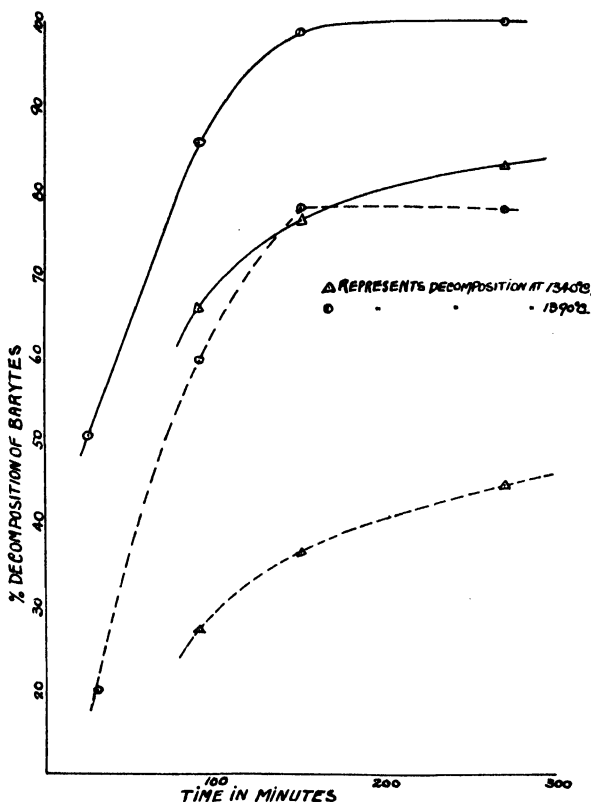
FIG. 3
Comparison of total decomposition (solid lines) and acid soluble barium (broken lines).

The last column in Tables III, IV, V and VI gives the molecular ratio Al_2O_3/BaO in the extract. It will be observed that in all cases except two (see Tables V and VI) the ratio is greater than unity.

When barytes is heated alone, it undergoes a slight decomposition due to the presence of small amounts of silica and Fe_2O_3. There seems to be a relation between the amount of decomposition and the solubility of the ferric oxide in acid. Thus, at 1140°C. the ratio BaO/Fe_2O_3 in the extract was 3.7 and at 1260°C. 2.7. It seems probable that there is produced tri-barium ferrite. No account was taken of the silica in these cases.

With mixture 3 (see Table V) the ratio Al_2O_3/BaO falls slightly below unity only after prolonged heating. If the amount of ferric oxide present in the extract is assumed to have come from tri-barium ferrite ($3BaO.Fe_2O_3$)

the ratio of the soluble alumina to the remainder of the soluble barium oxide becomes 1.009. The discrepancy in the case of Mixture 7 (Table VI) can be accounted for in the same way, the ratio Al_2O_3/BaO being increased to 1.112. It should be observed that in Mixture 7 there is an excess of alumina and that on prolonged heating the ratio BaO/Al_2O_3 increases to unity.

Within the temperature range 1000°C. to 1440°C. there is no evidence of the formation of tri-barium aluminate as claimed by G. W. Morey (loc. cit.).

W. Jander[1] has observed that in the reaction between $BaCO_3$ and WO_3 there is an excess of the latter in the acid-soluble extract over that required by the formula $BaO.WO_3$. He explains this by the assumption that WO_3 forms with the reaction product a solid solution which dissolves completely in the acid.

It is to be noted from the last column in Tables II, III and IV that on an average the mol ratio Al_2O_3/BaO in the extract approaches unity as the temperature is increased.

The solubility of the alumina in solid solution in barium aluminate either decreases with increase of temperature, or the dissolved alumina becomes more accessible to barium sulphate diffusing through the reaction product.

There seems to be some difference of opinion regarding the action of heat upon alumina. H. P. Rooksby[2] from an X-ray study of alumina at various temperatures found that from 200°C. to 500°C. γ-alumina was formed crystal growth occurring from 500°C. to 900°C. At 1150°C. the change to corundum was complete. E. Klever[3] by a combination of calorimetric and X-ray methods found that from 210°C. to 900°C. γ-alumina appears, the recrystallization to this form being complete from 900°C. to 1200°C. Above 1200°C. corundum begins to form. In Fig. 2 the time-decomposition curves at various temperatures for Mixture 5 are collected for comparison. It will be observed that, at 1182°C. and 1238°C., the slope of the curves at corresponding points is practically the same. The increased decomposition at 1238°C. is evidently due to the initial part of the reaction. Above 1238°C., however, a marked change occurs in the slope of the curves. This is better illustrated in Fig. 4 where the percentage decomposition is plotted against the logarithm of the time. W. Jander[4] identifies the beginning temperature of a reaction between two solids with the temperature at which one of them begins to crystallize—a process, he says, accompanied by increase in "solidity" (probably perfection of the crystal lattice) and decrease in volume. It is shown definitely here that the reaction was proceeding slowly in the vicinity of the temperature where the change from γ-alumina to corundum takes place. The marked acceleration of the reaction at 1340°C. and higher temperatures is probably due to the increased rate of change of γ-alumina to corundum.

[1] Z. angew. Chem., **41**, 73 (1928).
[2] Trans. Ceramic Soc., **28**, 399-404 (1929).
[3] Trans. Ceramic Soc., **29**, 149-161 (1930).
[4] Z. angew. Chem., **41**, 73 (1929).

Tammann[1] has observed that, in many reactions between solids, an apparent equilibrium is established. If the mixture be stirred or ground, the reaction proceeds a little further, but its rate is considerably diminished. He has shown (loc. cit.) that there can be no true equilibrium in reactions between solids when the heat of reaction is appreciable. J. Guillissen and Pierre J. Van Rysselberghe[2] have recently observed this phenomenon of

○ REPRESENTS DECOMPOSITION AT 1182°C
◇ " " " " 1238°C
△ " " " " 1840°C
× " " " " 1390°C
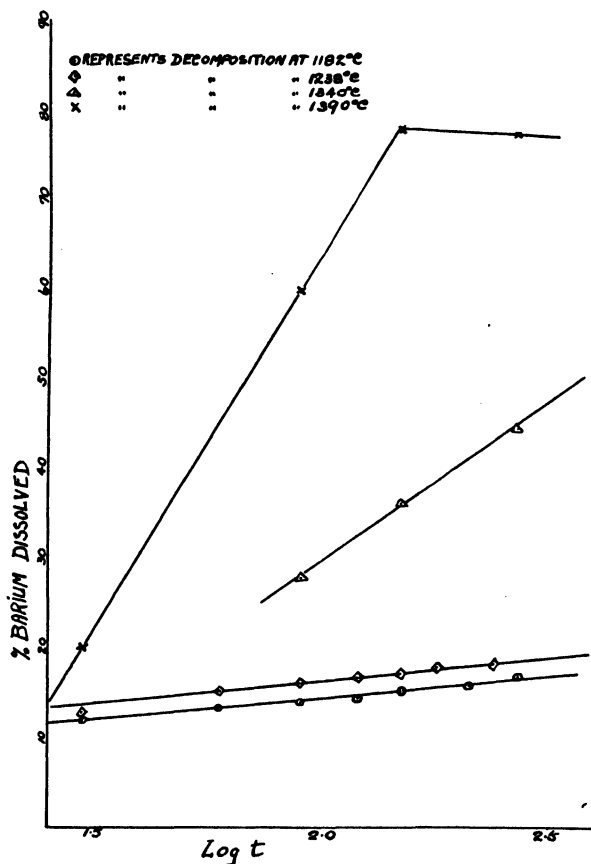
FIG. 4

% Barium rendered acid soluble plotted against log time

apparent equilibrium in the system $BaCO_3 + Fe_2O_3$. An equimolecular mixture ground so that it passed entirely through a 90 mesh sieve gave, on heating to 720°C. for nine hours, a decomposition of 77.2%. It was then ground so that it passed through a 150 mesh sieve and heated for 52 hours at the same temperature. The decomposition only increased to 89.32%. They explain this by assuming that the rate of diffusion had become extremely slow. They followed the course of the reaction by observing the loss in weight of the mixture.

[1] Z. angew. Chem., **39**, 869 (1926).

[2] Trans. Electrochem. Soc., April 1931 (Pre-print 59-1).

Reference to the curves in Fig. 2 for the decomposition in Mixture 5 at 1390°C. and 1440°C. shows that we have another case of apparent equilibrium. The curves show the percentage of barium in the mixture which dissolves in hydrochloric acid. The reaction appears to come to an abrupt end; indeed, on heating for three and one-half to four hours the percentage of soluble barium becomes a little less. Fig. 3 however, shows the true
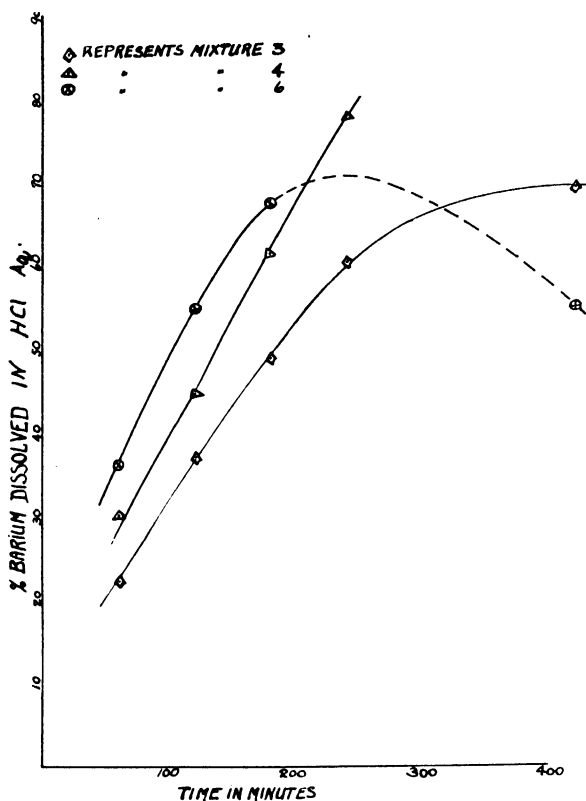
FIG. 5
Curve showing solution of barium aluminate in alumina

decomposition of the barium sulphate at 1340°C. and 1390°C. The broken lines show the percentage of barium rendered acid soluble. It will be observed that at the higher temperature the reaction goes to completion but that only 77.7% of the decomposed barium can be acid-extracted. With Mixture 7 (see Table VI and Fig. 6) at 1390°C. the percentage of soluble barium after seven hours heating was 91. This mixture contains a smaller excess of alumina than Mixture 5. With Mixture 3 (see Figs. 5 and 8) which contains an excess of barium sulphate, the reaction goes practically to completion when about 70% of BaSO$_4$ is decomposed. The barium aluminate formed is completely soluble in acid. The residue contains only 0.96% of the alumina. The above facts can be explained only by assuming the formation of a solid solution of barium aluminate in the excess of alumina.

In a recent paper Hedvall[1] and his co-workers show in Fig. 7 (page 420) the percentage decomposition in the mixture $CaO + NiCl_2$ plotted against the temperature. According to the curve there is more decomposition at 429°C. than at 461°C. The course of the reaction was followed by extracting the unreacted $NiCl_2$. This may be another example of solid solution interfering with the reaction progress. Unfortunately, however, the point at
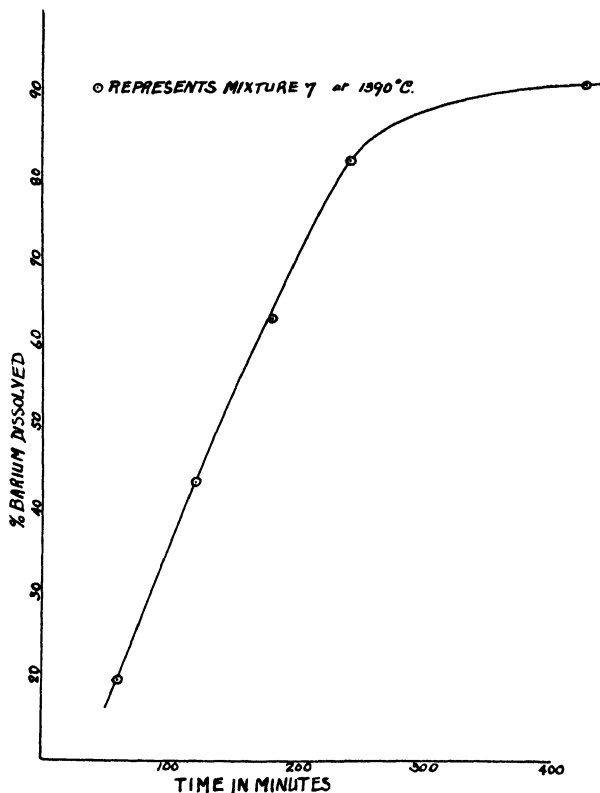
FIG. 6

% Acid soluble barium in mixture 7 at 1390°C

429°C. in their curve does not agree with their data in Table V from which presumably the curve was plotted. Perhaps this is a typographical error.

The question arises whether the solid solution of barium aluminate in alumina reaches saturation rapidly or whether the rate of diffusion of the aluminate into the alumina is comparable with the rate of reaction of the barium sulphate with the alumina. From the curve for Mixture 6 at 1370°C. in Fig. 5, it appears that after three hours 68% of the barium is soluble in acid while after seven hours only 55.5% is soluble. This indicates that, in this case, the decomposition of the barium sulphate is the more rapid. It is possible that the aluminate is soluble only in corundum and not in

[1] Z. anorg. Chem., **197**, 397 (1931).

γ-alumina and that after three hours at 1370°C. the transformation of the latter to corundum was not complete. The decomposition curve (Fig. 2) for Mixture 5 at 1440°C. indicates that the amount of aluminate in solution in the alumina decreases with the increase of temperature.

The formation of solid solutions in reactions between solids is of considerable interest from an industrial point of view. In the case of the reaction under consideration, it has been shown that, with an excess of alumina, some of the product is lost. The choice of the composition of the reaction mixture for maximum yield of soluble barium compounds must be governed by the temperature attainable and the time of heating.

Theoretical

The theory of reactions between solids has been developed principally by Tammann[1] and Jander[2] in Germany.

Hedvall[3] has also contributed considerably.

For some time it was believed that reactions did not proceed in the solid state but that, at the point of contact between two particles of the solids, fusion occurred. The reaction was then supposed to proceed in the melt. Others attributed the reaction to the presence of water vapour. It has been definitely established by the results of many investigators that neither of these conditions is necessary and that reactions take place in the solid phase. The following is a brief resumé of the theories:

Tammann (loc. cit.), from an examination of the reaction between CuO and WO_3, deduced that, in reactions between solids the rate of reaction depends upon the rate of diffusion of the two reactants through the reaction product and that the diffusion follows Fick's law.[4]

This law may be stated mathematically by the expression

$$dn = -Q.K. \, dy/dx \, dt \dots \dots \dots \dots (1)$$

Where dn = quantity of substance diffusing in time dt through a cross section of area Q parallel to a given surface and at distance x from it.

dy/dx = concentration gradient.

It has been shown experimentally that dy/dx = k/t

Where k is a constant.

Hence, from equation (1) we obtain

$$dn/dt = b/t \dots \dots \dots \dots \dots (2)$$

By integration of equation (2) Tammann derived the equation

$$n = b. \log. t + C \dots \dots \dots \dots (3)$$

[1] G. Tammann: Z. angew. Chem., **39**, 869 (1926).

[2] W. Jander: Z. anorg. Chem., **163**, 1 (1927); **166**, 31 (1927); **168**, 113 (1928); **174**, 11, 21 (1928); W. Jander and W. Stamm: **190**, 65, 397 (1930); **191**, 171 (1930).

[3] Z. anorg. Chem., **122**, 181 (1922); **128**, 1 (1923); **135**, 49 (1924); **140**, 243 (1924); **193**, 29 (1930).

[4] A. Fick: Pogg. Ann., **94**, 59 (1885).

From his experimental results on several reactions Tammann showed that by plotting the percentage decomposition against the logarithm of the time a straight line is obtained. The significance of the factor b in (3) according to Tammann is that it specifies the fraction of the "diffusion threads" which are broken at the time under consideration.

W. Jander (loc. cit.) has elaborated Tammann's views. He assumes that only one of the reactants diffuses. Integrating the expression

$$dy/dt = D\, C_o/y \dots\dots\dots\dots\dots\dots (4)$$

Where y = the thickness of the layer of reaction product
C_o = concentration of diffusing substance
D = diffusion coefficient
t = time

he obtains

$$y^2 = {}_2DC_o t \dots\dots\dots\dots\dots\dots\dots (5)$$

The relation between the thickness of the product layer and the percentage decomposition is given by

$$y = r\left(1 - \sqrt[3]{\frac{100-x}{100}}\right) \dots\dots\dots\dots\dots (6)$$

Where r = original radius of the particle (assumed to be spherical)
x = percentage decomposition

Combining (5) and (6) we have the following

$$\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2 = \frac{2DC_o}{r^2}\cdot t = Kt \dots\dots (7)$$

Jander[1] claims that a straight line is obtained by plotting

$$\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2 \text{ against t.}$$

The fraction of molecules reacting = $C.e^{-E/RT}$ and since the fraction of molecules reacting is proportional to D,

$$D = C.^{-E/RT}$$

Combining the constants D and C_o we have

$$K = C.e^{-E/RT} \dots\dots\dots\dots\dots\dots\dots (8)$$

Log K according to equation (8) should be a linear function of $1/T$. E is interpreted as the energy which a molecule must possess to break away from the crystal lattice.

In a study of the system $BaCO_3 + WO_3$ and $Ag_2SO_4 + PbO$, etc., Jander found that the time-decomposition curves fit the equation

$$\left(1 - \sqrt[3]{\frac{100-x}{100}}\right) = \frac{2.3}{C}\log t + \log b - \log\left(1 - \sqrt[3]{\frac{100-x}{100}}\right)^2 \dots (9)$$

Where b and C are constants.

[1] Z. angew. Chem., 41, 73 (1928).

Hume and his co-workers contribute the following ideas:

Three factors govern the course of a reaction between solids.

1. Rate of nucleus formation.
2. Linear rate of propagation of the interface between two solids.
3. The size of the reacting particles.

Transformation is essentially a change from a metastable crystal lattice to one of greater stability. If nucleus formation is very rapid compared with the linear rate of propagation, the fraction α decomposed in unit time[1] is

$$\alpha = 3 \, (ut/a) - 3 \, (ut/a)^2 + (ut/a)^3 \dots\dots\dots\dots\dots\dots\dots\dots(10)$$

If the particle develops only a small number of nuclei before the interface travels over the whole surface, then

$$\alpha = (ut/a)^{3/2} - 3/16 \, (ut/a)^4 \dots\dots\dots\dots\dots\dots\dots\dots(11)$$

If the linear rate of propagation of the interface is so great that a particle may be regarded as completely decomposed as soon as it develops a nucleus, then rate of decomposition $= k_o \, N_t$.

Where $k_o =$ number of nuclei formed per second
$N_t =$ number of undecomposed particles present at time t.

This represents a pseudo monomolecular reaction and should be fulfilled by small particles. All reactions should approach this form on reducing the particle size.

These views have been tested experimentally with the transformation $S_{monoclinic} \rightleftarrows S_{rhombic}$ which was shown to have a monomolecular constant

$$K = 1/t \cdot \log \frac{h_o}{h_o - h_t} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(12)$$

The reaction was followed dilatometrically and

$h_o =$ the total contraction of the water column
$h_t =$ the contraction of the water column after time t.

It is interesting to see how the reaction between barium sulphate and alumina fits into these theories. Tammann's equation (3) lends itself to a simple test. When the percentage decomposition is plotted against log t, a straight line should be obtained. In Fig. 4 the curves obtained in this manner are shown to be straight lines within the limits of the experimental error. At the lower temperatures, 1182°C. and 1238°C., a very good corroboration of Tammann's law is obtained. At the higher temperatures, 1340°C. and 1390°C. only three points on each curve were determined. In Fig. 7, however, similar curves for Mixtures 3 and 7 at 1370°C. and 1390°C. respectively show considerable deviation from a straight line. It is possible that the straight lines obtained in Fig. 3 for temperatures 1340°C. and 1390°C. may

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[1] J. Hume and J. Colvin: Phil. Mag., (7), **8**, 589 (1929); Topley and Hume: Proc. Roy. Soc., **120A**, 211 (1928).

be fortuitous.   Fig. 8 shows the percentage of alumina rendered soluble plotted against the log t.   The same type of curve is obtained as in Fig. 7. Straight lines have been drawn through the points, and it can be seen that the experimental points do not lie very close to them.   In applying Jander's equation (7) the data given in Table VII are used.   The squares of the values
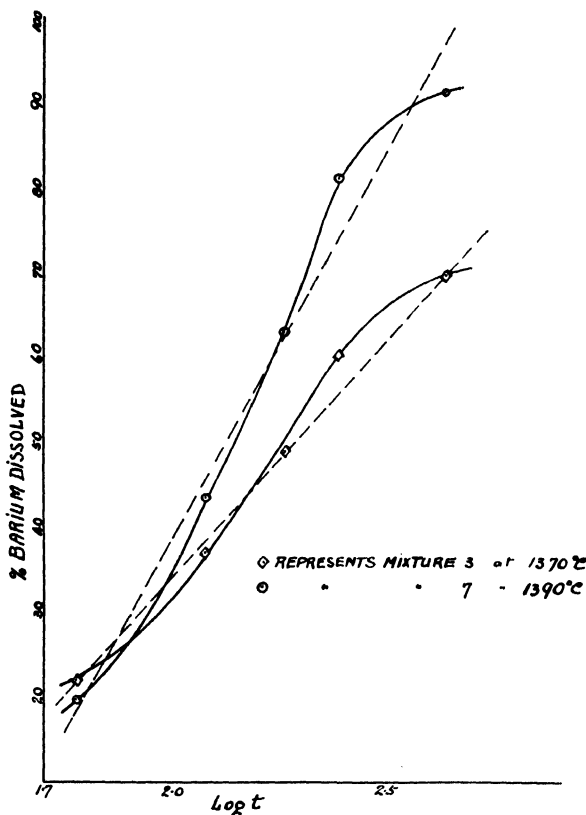
FIG. 7

% Barium dissolved in HCl aq. plotted against log time for mixtures 3 and 7 showing deviation from Tammann's equation

of $\left(1 - \sqrt[3]{\dfrac{100-x}{100}} \right)$ are plotted against t in Fig. 9.   The values of the squares

of $\left(1 - \sqrt[3]{\dfrac{100-x}{100}} \right)$ calculated from the straight lines in Fig. 8 are represented

by crosses.   It should be observed that all the experimental points for Mixture 3 lie on a smooth curve and that the first four points for Mixture 7 lie on a similar curve.   The crosses for the first four points lie fairly close to a straight line but the fifth point in each case is very far out of line.

Fig. 10 shows the application of Jander's equation to the reaction at 1182°C. and 1238°C.   The first part of the curve is very steep, representing
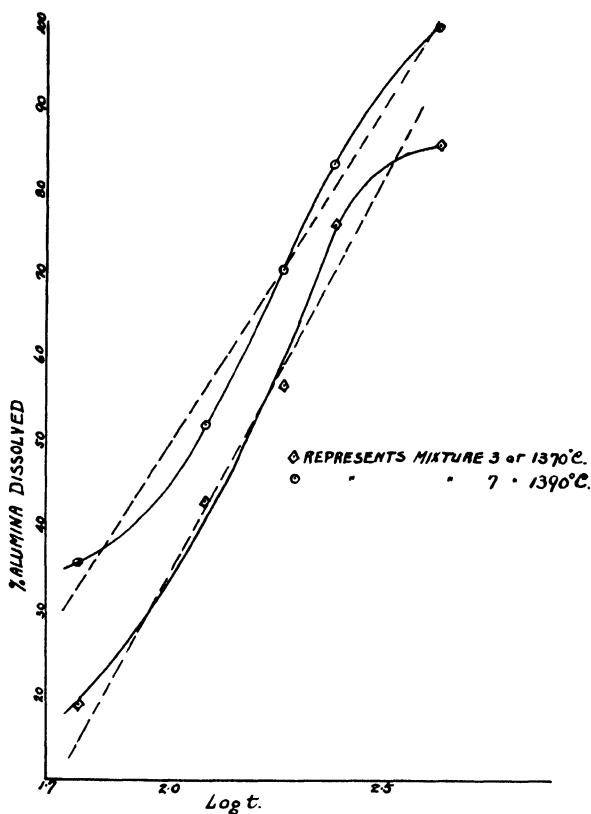
Fig. 8

% Alumina dissolved in HCl aq. plotted against log time for mixtures 3 and 7
showing deviation from Tammann's law

TABLE VII

Mix.	Time in minutes	log t	% Al$_2$O$_3$ soluble	$\left(1-\sqrt[3]{\dfrac{100-x}{100}}\right)$ experimental	$\left(1-\sqrt[3]{\dfrac{100-x}{100}}\right)$ from str. line	$\log\dfrac{100}{100-x}$
	60	1.7782	35.77	0.137	0.121	0.192
	120	2.0792	52.35	0.219	0.239	0.322
3	180	2.2553	70.60	0.332	0.335	0.532
	240	2.3802	82.90	0.445	0.415	0.766
	420	2.6232	99.04	0.789	0.829	2.018
	60	1.7782	18.95	0.068	0.049	0.091
	120	2.0792	40.31	0.158	0.171	0.224
7	180	2.2553	56.77	0.244	0.257	0.363
	240	2.3802	75.77	0.377	0.327	0.616
	420	2.6232	85.33	0.473	0.560	0.834
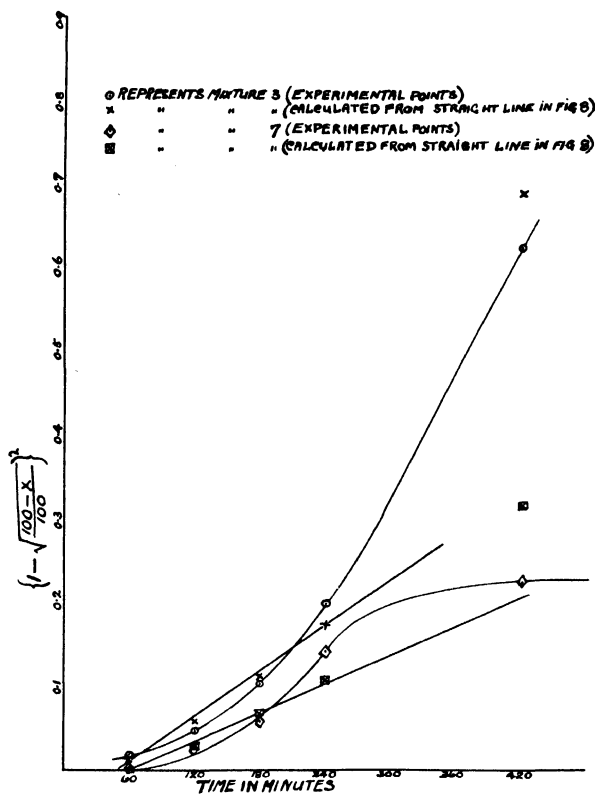
FIG. 9

Jander's equation applied to % Alumina rendered HCl aq. soluble

TABLE VIII

Mixture Number 5

Temp.	Time in minutes	X	$\left(1 - \sqrt[3]{\dfrac{100-x}{100}}\right)^2$
1182°C.	30	11.90	.00170
	60	13.29	.00214
	90	13.87	.00232
	120	14.49	.00257
	150	15.30	.00290
	210	15.85	.00313
	270	16.60	.00360
1238°C.	30	12.87	.00203
	60	15.29	.00290
	90	16.32	.00333
	120	16.99	.00361
	150	17.27	.00373
	180	17.65	.00392
	240	18.10	.00415

the rapid initial reaction which takes place at the points of contact between the barium sulphate and alumina particles or perhaps results from the diffusion of the barium sulphate over the surface of the alumina particles. The straight line represents the reaction due to the diffusion of the barium sulphate through the reaction product.
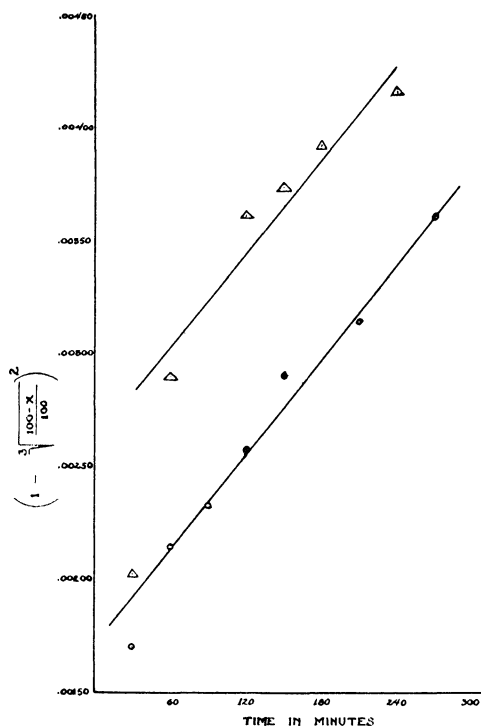
Fig. 10

Jander's Equation applied to Mixture No. 5. See Table VIII

In all cases considered the amount of soluble barium or alumina depends upon two factors:

(a) the diffusion of the barium sulphate through the aluminates,

(b) the diffusion of the aluminate into the alumina.

The type of curves obtained can be explained by assuming that the solution of the aluminate in the alumina reaches saturation before the completion of the reaction. This results in an apparent acceleration of the reaction.

From the derivation of Tammann's and Jander's equations, however, it is obvious that they can only be applied so long as Fick's law is applicable and so long as the reaction rate depends upon diffusion. It is possible that at temperatures above 1238°C. the reaction rate is no longer controlled by diffusion but that the crystallographic change from γ-alumina to corundum is the chief factor.

It was observed that by plotting the value of $\left(1 - \sqrt[3]{\dfrac{100-x}{100}}\right)$ against t, a straight line is obtained (see Fig. 11). The crosses again indicate the values calculated from the straight lines in Fig. 8.

Equation (12) has been subjected to a similar test. The curves obtained are shown in Fig. 12. They appear to be parallel in the lower part where

FIG. 11

$\left(1 - \sqrt[3]{\dfrac{100-x}{100}}\right)$ plotted against time

they deviate considerably from a straight line. The upper curve represents Mixture 3 in which the alumina disappears almost completely after seven hours. The lower curve represents Mixture 7 in which there remains an appreciable quantity of alumina after the reaction is complete.

From the shape of the upper curve in Fig. 12, it can be seen that a straight line must be approached after 83% of the alumina has reacted. This is a confirmation of the statement of Hume and Colvin (loc. cit.).

In conclusion we may say that Tammann's and Jander's equations are applicable to this reaction at temperatures below 1238°C. At higher temperatures there is an apparent deviation from the theoretical curve which may be explained by the cessation of one of the diffusion processes. The deviation may also be due to the crystallographic change of the alumina from γ-alumina to corundum. The monomolecular equation of Hume and Colvin seems to be applicable after 83% of the alumina has reacted.
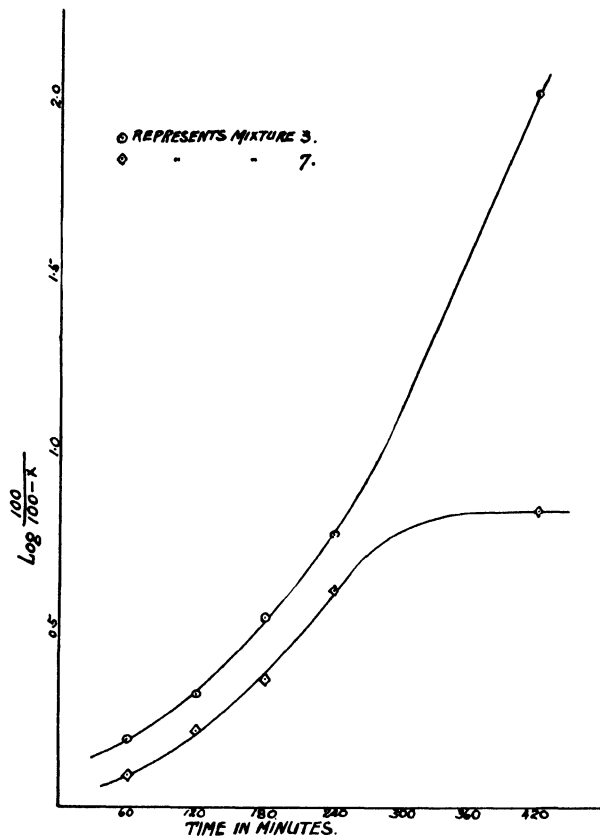
FIG. 12

Application of Hume and Colvin's equation to the reaction between BaSO$_4$ and Al$_2$O$_3$

Acknowledgment

Summary

1. Reaction between barium sulphate and alumina takes place appreciably at temperatures above 1000°C.

2. The reaction rate increases with increasing proportions of alumina in the reaction mixture.

3. The reaction will not go to completion at temperatures below 1238°C.

4. The temperature at which rapid reaction sets in is close to that at which γ-Alumina changes to corundum.

5. The percentage of barium rendered soluble is not always a true measure of the decomposition attained. When the reaction mixture contains an excess of alumina, some of the barium aluminate forms with it a solid solution which is insoluble in hydrochloric acid.

6. The reaction product at temperatures between 1000°C. and 1440°C. is mono-barium aluminate $BaO.Al_2O_3$. No evidence for the formation of tri-barium aluminate was obtained. The mono-barium aluminate produced is water soluble and sulfur free and may be used in the production of pure barium compounds.

7. The mechanism of the reaction between barium sulphate and alumina involves the following processes:

(1) Initial rapid reaction at the points of contact between the barium sulphate and alumina particles. The latter part of this rapid reaction may also be due to the diffusion of the barium sulphate over the surface of the alumina particles.

(2) Slower reaction due to the diffusion of the barium sulphate through the layer of reaction product, mono-barium aluminate.

(3) Diffusion of the reaction product into the alumina.

(4) Crystallographic change of γ-alumina to corundum.

The rate of reaction increases (a) with increase of proportion of alumina in the mixture, and (b) with the rapidity of the change of γ-alumina to corundum.

The amount of barium aluminate which can be extracted at any time during the progress of the reaction depends upon the relative rates of (2) and (3).

The amount of barium aluminate which can be extracted after the completion of the reaction varies inversely with the excess of alumina.

Tammann's and Jander's equations are applicable to the slower reaction occurring below 1238°C. The deviation from the theoretical curves at higher temperatures is probably due to (3) reaching completion which results in an apparent acceleration of the reaction. The fact that the change of γ-alumina to corundum has some influence upon the reaction rate may also be responsible for the deviation since the reaction evidently does not depend wholly upon Fick's law of diffusion.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.

A STUDY OF ENERGIES OF IMMERSION OF SILICA IN A SERIES OF LIQUIDS

BY F. E. BARTELL AND E. G. ALMY[1,2]

Introduction

The determination of the surface energy of solid-air and of solid-liquid interfacial systems constitutes a problem of outstanding importance to colloid chemistry. The problem has received a great deal of attention, but to date no reliable values for the surface energy of either of these classes of systems have been obtained. It is possible, however, to approach the problem of the energy relation at solid surfaces from the standpoint of energy changes occurring at such surfaces. When a solid is immersed in a liquid the original solid-air interface is replaced by a solid-liquid interface and an energy change occurs. This energy change, which may be called the energy of immersion, has been investigated in several different ways and values for such changes have been obtained. For the sake of clarity, a discussion of the energy changes may be divided into considerations of free surface energy changes and total surface energy changes.

Free Surface Energy Changes

When a solid is immersed in a liquid the solid-air interface disappears and an equal area of the interface solid-liquid results. We may designate the surface tension of the solid by the symbol S_1 and the interfacial tension between solid and liquid by S_{12}, and since the surface tension and the interfacial tension are equal numerically to the free surface energies of the systems solid-air and solid-liquid respectively, the free energy change per unit area upon immersion is represented by the expression, $S_1 - S_{12}$. This expression, however, is the same as that which has received treatment under the heading of "Adhesion Tension." Numerically, the adhesion tension, A_{12}, of a system represents the difference between the surface tension of a solid and the interfacial tension of the solid against a given liquid, that is, $S_1 - S_{12} = A_{12}$. The adhesion tension of a solid-liquid system may be readily evaluated if the liquid forms a contact angle with the solid. The existing relation is given by the equation of Thomas Young:[3]

$$S_1 - S_{12} = S_2 \cos \theta.$$

If the surface tension of the liquid is known, it is necessary to determine only the contact angle which the liquid forms with the solid, when at equilibrium, in order to calculate the adhesion tension which in turn should be numerically

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[1] The material presented in this paper is from a dissertation submitted by E. G. Almy to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, February 1932.

[2] Holder of du Pont Fellowship, 1930-31.

[3] Thomas Young: Phil. Trans., **1805**, 84.

equal to the free energy of immersion. One of the objects of the present paper is to show that the adhesion tension as determined by measurement of contact angles is in fact equal to free energy of immersion as calculated from heat of wetting data. Any of several methods may be used in measuring the contact angles to be used in calculating adhesion tension. A discussion of the various methods used for determining contact angles is to be published shortly in a paper from this laboratory. Such methods will not, therefore, be discussed in this paper.

Direct measurements of the free energy change upon immersion have been attempted by Tangl[1] and by Röntgen,[2] the method in each case being based upon a determination of the deformation of a film of the solid (such as a rubber membrane) when it was coated with the liquid. Such a method is applicable to liquids that form zero contact angles with the solids as well as to those that form finite contact angles. This method has two very serious defects: (1) The number of solids that can be obtained in the form of suitable membranes is very limited, and, (2) the measurements are very inaccurate.

The displacement pressure method for the measurement of adhesion tension of contact angle liquids has been extended to include the measurement of adhesion tensions of liquids which form zero contact angles with the solid. By this means the adhesion tensions of a fairly large number of solid-liquid systems have been determined. In this work it was necessary that the solid to be studied be one that could be reduced to powder. The method involves the determination of solid-liquid-air contact angles and of solid-liquid-liquid interfacial contact angles by means of displacement pressure measurements. A detailed description of the method and of the calculation employed is to be found in recent literature.

Total Surface Energy Changes

The total energy of immersion, the change in total energy which occurs when a solid-air interface is replaced by a solid-liquid interface, may be determined by measuring the heat of wetting. If E_1 be taken to represent the total energy per unit area of the solid-air interface and E_{12}, the total energy of the solid-liquid interfaces, the expression, $E_1 - E_{12}$, will represent the total energy of immersion. The relation between the free and total surface energies is given by an equation of the Gibbs-Helmholtz type,

$$E = S - TdS/dt$$

the second term of the right hand member representing the latent energy of the system.

The heats of wetting of various substances have been investigated and recorded by several authors who have not attempted to calculate the surface energy changes involved. Herbst[3] has tried to correlate the heats of wetting of certain active charcoals with their various physical properties. Kobayashi

[1] Tangl: Ann. Physik, (4) **34**, 311 (1911).
[2] Röntgen: Wied. Ann., **3**, 324 (1878).
[3] Herbst: Kolloid-Z., **38**, 314 (1926).

and Yamamoto[1] have utilized this quantity in estimating the relative surface areas of adsorbent clays. Bouyoucos[2] has used the heat of wetting as a means of estimating the colloid content of soils. The large specific surface of colloids assures that the amount of colloids in soils is approximately proportional to the heat of wetting. Grimm, Raudenbusch, and Wolff[3] have compared the heats of wetting of silica gel by various liquids with the preferential adsorption of those liquids by the gel, particularly as it might apply to the separation of binary liquid mixtures by silica. Landt[4] has used heat of wetting data as a means of estimating the relative surface areas of adsorptive carbons.

A few researches have been conducted in which attempts have been made to calculate surface energy changes. It has been pointed out[5] that no matter what the mechanism of wetting, the heat developed is a measure of the decrease in total surface energy when the solid-air interface is replaced by a solid-liquid interface. Using the microscope to determine the specific surface of the powder, Harkins and Dahlstrom[6] were able to estimate the energy of immersion per sq. cm. of crystalline TiO_2 in each of several liquids from heat of wetting data. Inasmuch as they believed that the microscopic method gave too small an area, they arbitrarily multiplied the measured specific area by two. They do not fully justify the choice of this particular factor and, as a result, the absolute magnitudes of their calculated energies can hardly be considered to be exact. The relative values of their energies of immersion are probably correct. Koehler and Mathews[7] found the heat of wetting of $PbSO_4$ by water to be less than their experimental error. They had estimated the area of the solid by a radioactive indicator method and so were able to conclude that the decrease in total surface energy when dry $PbSO_4$ is wet by water is less than 71 ergs/cm². Patrick and Grimm[8] determined the heats of wetting, by each of several liquids, of silica gel containing water. They assumed that such a gel presented an all water surface to the wetting liquid and, on that basis, calculated the area of surface so exposed. For several liquids they obtained good agreement of area, but they were unable to explain satisfactorily the high heats of wetting of water miscible liquids.

Bartell and Fu[9] have shown that, with the aid of certain assumptions, it is possible to relate adhesion tension to the total energy change per sq. cm. when a solid is immersed in a liquid. This treatment permits of the estimation of the specific surface area of the solid from heat of wetting data and, in consequence, makes possible the determination of the energy relations at the solid-liquid interface for those liquids that cannot be studied by the displace-

[1] Kobayashi and Yamamota: J. Soc. Chem. Ind. Japan, 31, 434 (1928).

[2] Bouyoucos: Soil Science, 19, 153 (1925).

[3] Grimm, Raudenbusch, and Wolff: Z. angew. Chem., 41, 104 (1928).

[4] Landt: Z. Vereins. deutsch. Zucker Ind., 79, 44 (1929).

[5] Bartell and Fu: Colloid Annual, 7, 135 (1920).

[6] Harkins and Dahlstrom: Ind. Eng. Chem., 22, 897 (1930).

[7] Koehler and Mathews: J. Am. Chem. Soc., 46, 1158 (1924).

[8] Patrick and Grimm: J. Am. Chem. Soc., 43, 2144 (1921).

[9] Bartell and Fu: loc. cit.

ment pressure method (water miscible liquids). In their preliminary measurements, these investigators found good agreement between the theory and the experimental values obtained.

It is with this relation between adhesion tension, which should be numerically equal to the free energy of immersion, and the total energy of immersion as measured by the heat of wetting, that this paper is primarily concerned. It is essential to the development of the mathematical relation between these quantities that the heats of wetting of two different samples of silica by any one liquid be proportional to the surface area of the two samples. A survey of the literature on heats of wetting of silica gel would indicate that the values of heats of wetting by the same liquid are very different for different samples of gel and that the heats of wetting of one gel by a series of liquids bear no definite relation to the heats of wetting of another gel by the same series of liquids. The first of these differences is easily explained by assuming that the gels used by different investigators presented different specific surface areas. We had reason to believe, however, that if the heats of wetting of one silica gel by each of two liquids stood in a certain ratio, the heats of wetting of another sample of silica by the same two liquids should stand in the same ratio and that the disagreement in such relative values found in data from the literature was due to experimental error of one kind or another. The first object, then, in the present investigation was to compare the heats of wetting of various preparations of silica by several liquids to determine whether or not the ratio of the heats of wetting of the gel by liquid A and by liquid B is the same for all samples of silica.

If such a constancy of ratios is found it may be concluded that the relative heats of wetting represent very closely the relative total energies of immersion. We have already indicated that total energies of immersion can also be calculated from adhesion tension data. These values can then be reduced to a relative basis and a comparison made between the relative total energies measured by heats of wetting and relative total energies calculated from adhesion tension data. Agreement between the two sets of values would indicate that the adhesion tension values represent free energies of immersion and that it is possible to calculate free energies of immersion from total energies of immersion, or the reverse, i.e., it is possible to calculate total energies of immersion from free energy of immersion data obtained from adhesion tension measurements.

Experimental

Apparatus: The calorimeter used and the procedure followed in the heat of wetting determinations have been described in an earlier paper.[1]

Materials: Silica gel prepared as described in the earlier paper was used in this investigation and designated as Silica A.

Silica B was a commercial silica gel which was refluxed with nitric acid for several hours and then washed until free from acid. It was a harder gel than Silica A and seemed to be more active.

[1] Bartell and Almy: J. Phys. Chem., **36**, 475 (1932).

Silica C was prepared by neutralizing sodium silicate (specific gravity 1.025) with hydrochloric acid (1:1). After the mixture had set to a gel it was placed in a refrigerator at − 15°C., and allowed to stand for forty-eight hours. This freezing process broke down the gel as surely and much more rapidly than slow drying, so that upon thawing, the active silica could readily be washed free from salts and acid. The product was very soft and could be crushed to a powder easily. Its activity was about the same as that of Silica B.

The liquids used were carefully purified to insure the absence of capillary active substances.

Water: Conductivity water was used throughout.

Nitrobenzene: The nitrobenzene was washed with acid and dried over K_2CO_3. It was then distilled with steam and redistilled in vacuo. It was then fractionated at atmospheric pressure, the portion boiling at 210.9 ± .1°C. being retained. Finally it was recrystallized twice. The freezing point was 5.60 ± .02°C. It was stored in a flask that contained a tube of P_2O_5.

Benzene: Baker's C. P. Benzene was washed with acid and with alkali and refluxed over successive portions of mercury until the surface of the latter remained bright. It was then fractionally crystallized, the portion freezing at 5.48 ± .02°C. being retained. This was distilled from P_2O_5 to dry the product. Its boiling point was 82.20 ± .01°C.

Chlorbenzene: Carefully purified chlorbenzene was used. Its boiling point was 132.01°C., and its density 1.1008 at 25.13°C.

Ethyl Benzene: Eastman's best grade of ethyl benzene was fractionally distilled from P_2O_5, the fraction boiling at 136.10° − 136.13°C. being retained.

Chloroform: Mallinckrodt's C. P. chloroform was found not to discolor mercury on shaking nor to precipitate with silver nitrate in water solution. It was distilled from P_2O_5 to remove any trace of alcohol or moisture, and the fraction distilling over at 61.18°C. was stored in a dark-colored glass-stoppered bottle.

Carbon tetrachloride: A good grade of carbon tetrachloride was washed with sulfuric acid and with alkali, dried over fused KOH and shaken with successive portions of mercury until the surface of the latter was no longer darkened by contact with the liquid. It was finally fractionally distilled from P_2O_5, the fraction coming over at 76.75°C. being retained.

Hexane: Synthetic hexane from Eastman Kodak Co. was further purified by shaking with concentrated sulfuric acid, then with alkaline permanganate and finally with acid permanganate. It was dried over fused KOH and distilled fractionally from P_2O_5. A middle fraction boiling at a constant temperature of 68.80°C. was collected and used.

Measurements and Results:

The importance of the removal of capillary active impurities from the liquids used is made evident by the data for the heat of wetting by benzene containing varying amounts of water (Table I). It is seen that mere traces of water may raise the heat of wetting of benzene by as much as 50%. For this

reason the following precaution was observed. Just before closing the calorimeter at the beginning of each determination a small amount of activated silica was dropped into the liquid contained therein. This treatment removed any traces of moisture that may have been introduced during the transfer of the liquid to the calorimeter.

TABLE I

Heats of Wetting by Benzene containing Varying Amounts of Water

Per cent water	Heat of wetting
0.000	10.64 cal./gm.
.015	13.47
.030	14.96
.059	17.07

A series of heats of wetting by water, by nitrobenzene, and by benzene on samples of silica A of widely different water contents and activities were determined. The differences in activity and in water content were induced by varying the temperature and time of activation treatment as described in the earlier paper. The results are collected in Table II. Q_w, Q_n, and Q_b represent the heats of wetting by water, nitrobenzene, and benzene, respectively.

TABLE II

Heats of Wetting of Gels of Differing Water Contents by Water, Benzene and Nitrobenzene

$\dfrac{\text{Mols } H_2O}{\text{Mols } SiO_2}$	Q_w	Q_b	Q_b/Q_w	Q_n	Q_n/Q_w
0.18	13.8	—	—	10.3	.75
.15	17.0	12.1	0.71	13.4	.79
.14	17.0	11.7	.69	15.0	.88
.13	18.3	12.2	.67	14.5	.79
.11	17.9	11.2	.63	14.1	.79
.11	17.8	11.8	.65	13.9	.78
.097	19.3	12.4	.64	14.5	.75
.094	16.1	10.8	.67	13.1	.81
.089	17.2	11.2	.65	13.5	.78
.060	17.0	11.1	.65	12.5	.74
.048	14.3	9.3	.65	11.6	.81
.042	13.8	9.6	.69	11.5	.83
.019	9.4	6.3	.67	7.8	.83
			Av. .66 ± .02		Av. .80 ± .02

It was noticed that with all these samples of silica the ratios Q_b/Q_w, and Q_n/Q_w were constant to within a few per cent, and it was deemed advisable to determine whether this same condition would prevail with other liquids and with samples of silica prepared in entirely different manners. For this reason, Silica B and Silica C were prepared as above described, and the heats of wetting by several liquids determined for samples of each of these types, and also

for another sample of Silica A. The activation treatment in each case was to heat at approximately 250°C. for three hours. Table III shows the data obtained for determining the heats of wetting, and in Table IV the results are summarized.

TABLE III

Details of Heats of Wetting Determination

Liquid	Heat Cap. of System	Wt. Sample of Gel	ΔT	$-Q$	
Silica A.					
Water	66.91	.8515	.240	18.86	
	66.82	.6706	.187	18.63	
					18.75
Acetone	32.88	.4541	.287	20.78	
	32.88	.5308	.336	20.82	
					20.80
Ethyl-	29.62	.6286	.230	10.84	
Benzene	29.76	.8497	.310	10.86	
					10.85
Chloroform	29.43	.6587	.234	10.45	
	29.43	.6554	.228	10.24	
					10.35
Silica B.					
Water	66.86	1.1920	.435	24.42	
	66.86	1.6829	.618	24.48	
					24.45
Acetone	33.17	.9047	.706	25.89	
Ethyl-	30.47	1.0534	.478	13.83	
benzene	31.06	.7373	.324	13.65	
					13.74
Chloroform	29.39	1.2332	.558	13.30	
	29.39	.7771	.350	13.24	
					13.27
Silica C.					
Water	66.70	.8826	.296	22.37	
	67.27	.6783	.225	22.31	
					22.34
Acetone	33.28	.5312	.318	23.87	
	32.42	.4963	.366	23.90	
					23.89
Ethyl-	29.62	.6569	.267	12.04	
benzene	29.71	.4788	.189	11.73	
	29.71	.6306	.262	12.34	
	29.58	.5859	.232	11.71	
					11.95
Chloroform	29.00	.5271	.214	11.77	
	29.93	.5498	.217	11.82	
					11.80

TABLE IV

(Summary of Table III)

Heats of Wetting of Three Silicas by Four Different Liquids

Silica. Heat of wetting by:

	Water	Acetone	Ethyl benzene	Chloroform
A	18.75	20.80	10.85	10.35
B	24.45	25.89	13.74	13.27
C	22.34	23.89	11.95	11.80

The ratios of the heats of wetting of silica A were determined for these liquids and compared with the ratios of the heats of wetting of silicas B and C. The values are shown in Table V in which the symbols not previously defined

TABLE V

Ratios of Heats of Wetting of Different Silicas by Different Liquids

Silica	Q_a/Q_w	Q_e/Q_w	Q_c/Q_w
A	1.06	0.58	0.55
B	1.11	0.54	0.54
C	1.07	0.56	0.53
	1.08	0.56	0.54

are Q_a, Q_e, and Q_c for heats of wetting by acetone, ethyl benzene and chloroform, respectively. Again it is observed that while the absolute values for heats of wetting may vary from one sample of silica to another, the relative values of the heats of wetting by a series of liquids are the same as we pass from one sample of silica to another even though those samples may vary widely in their physical properties, activity, and methods of preparation.

Since the ratio of heats of wetting by two liquids is then largely independent of the sample of silica used, the heats of wetting by other liquids than those already discussed may be determined on new samples of silica and reduced to a basis comparable with the others if the heats of wetting by a reference liquid, such as water, be determined for each sample of silica used. In Table VI are

TABLE VI

Heats of Wetting by Three Organic Liquids compared to Heats of Wetting by Water

Gel sample	Q_{water}	$Q_{organic\ liquid}$	Ratio Q_o/W_w
A_1	18.0	11.3 Chlorbenzene	.62
A_1	18.0	6.6 n-Hexane	.37
A_2	16.1	7.3 Carbon tetrachloride	.45
A_3	14.3	6.4 Carbon tetrachloride	.45

shown the heats of wetting of a few liquids for samples of silica of such activity that the heats of wetting by water are those shown in the second column. The liquids reported in this table were chosen because some of the most reliable

adhesion tension data available were obtained for these same liquids against silica. The total energies of immersion found experimentally from heats of wetting of these liquids by silica can then be compared with those calculated from the adhesion tension data available for these liquids against silica.

Discussion of Results

Ratios of Heats of Wetting of Different Gels:

It has been pointed out that the data to be found in the literature on the heats of wetting of silica gel are highly discordant as regards both absolute values and relative values. The present work has shown, however, that the relative values of the heats developed when exactly similar samples of gel are wet by a series of liquids are always the same; i.e., for any sample of silica the heat of wetting by benzene is .66 times that by water, while that by acetone is 1.08 times that by water, etc.[1] It is essential only that the samples of silica wetted by the liquids to be compared be uniform in surface area, a condition that requires careful control of experimental methods.

We can now with justification reduce the heats of wetting of silica by all the liquids studied to a comparable basis even though no one sample of silica was used throughout the entire series of liquids. Since the ratios of heats of wetting by different liquids are constant we can arbitrarily set the heat of wetting by a reference liquid equal to unity and calculate the heats of wetting by the other liquids for the same sample of silica. If benzene be chosen as the reference liquid ($-Q = 1.00$) the relative values of the heats of wetting by all the liquids are shown in Table VII. Now, if the heat of wetting of a given gel by

TABLE VII

Relative Heats of Wetting of Silica by Nine Different Liquids. (Benzene = 1)

Liquid	$-Q$	Liquid	$-Q$
Acetone	1.64	Ethyl benzene	.85
Water	1.51	Chloroform	.82
Nitrobenzene	1.21	Carbon tetrachloride	.69
Benzene	1.00	Hexane	.56
Chlorbenzene	.94		

any of the liquids in this series is known, the heat of wetting by any of the other liquids is easily calculated. It is necessary only to multiply by the appropriate conversion factor, which factor can readily be obtained from the ratio values in the table.

From the fact that the ratio of the heats of wetting of silica gel by two liquids is constant though the water content of the gel is varied, some interesting conclusions can be drawn concerning the part played by the gel water in the energy changes occurring when the gel is immersed in a liquid. This is a

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[1] In the results on heats of wetting of charcoal reported by Herbst (loc. cit.) a similar effect may be noticed although he did not specifically call attention to it. An examination of his data shows that for five different samples of activated charcoal being wet by water and by benzene, the quotient Q_w/Q_w was 0.751 ± .003.

subject over which there has, in the past, been considerable controversy. It has been shown[1] that the water cannot be present as a continuous film, thus exposing an all-water surface to the wetting liquid. This leaves one of two alternatives, (1) the area of the water surface must be so small in comparison to the surface of the silica that it may be ignored, or (2) the gel must present a composite surface of silica and water, the proportion of solid to liquid changing as the water content changes. The following equations would seem to present sufficient evidence to justify the conclusion that the ratio of the heats of wetting of the water containing gel by two liquids is the same as the ratio of the heats of wetting of dry silica by the same two liquids.

The following expression may be used to represent the energy changes which occur when unit area of the composite surface is immersed in a liquid:

$$xa + (1-x)b = q_1$$

in which, for unit area of gel x is the area fraction of silica and $(1-x)$ is the area fraction of water surface. a and b are the energy changes which occur when the silica and water, respectively, are immersed in the liquid. q is the heat evolved. If another sample of the same gel be immersed in another liquid the analogous expression is:

$$xc + (1-x)d = q_2.$$

Dividing one equation by the other we obtain:

$$\frac{xa + (1-x)b}{xc + (1-x)d} = \frac{q_1}{q_2}$$

In this expression, a, b, c, and d are fixed quantities for any pair of liquids; x may have any value from 0.0 to 1.0. But the right hand member of the equation, q_1/q_2 is the ratio of the heats of wetting of the gel by the two liquids and is the quantity which, we have seen, remains constant though the water content varies. It follows that the left hand member of the equation above must remain constant for all possible values of x. This can be true only if $a/c = b/d = q_1/q_2$. We can conclude, then, that the ratio of the heats of wetting, q_1/q_2, of the gel, even though it contains some water, is the same as the ratio of the total energies of immersion of the dry silica, a/c. It is also evident that one of two postulates must explain the part played by the gel water. Either (1) the water must be so contained that its exposed surface area is negligibly small in comparison with the area of the solid, or (2) the ratio of energies of immersion of silica in two organic liquids has the same value as the ratio of the energies of immersion of water in the same two organic liquids.

The evidence obtained in a study of water content of activated silica[1] indicates that the first of the two postulates probably represents the actual condition within the gel. The residual water is thought to be confined in the finest of the gel micropores and to be practically surrounded by silica. The area exposed therefore should be relatively small. Evidence that the statement in the second postulate represents a general relation between organic liquids at

[1] Bartell and Almy: J. Phys. Chem., **36**, 475 (1932).

the surface of water and at the surface of a polar solid has been presented by Harkins and Dahlstrom[1] and by Bartell and Hershberger.[2] It follows that even though the gel should expose an appreciable area of water surface that the constancy of ratio would be observed. It is probable, however, that the first postulate is sufficient to explain the heat of wetting relationships between differing silicas and a series of liquids.

Comparison of Observed Ratios and Ratios calculated from Adhesion Tension Data:

The relation between adhesion tension and heat of wetting as developed by Bartell and Fu is expressed by the following equation:

$$-Q = a(A_{12} - KT \; dS_2/dT)$$

where a represents the area of the solid; A_{12}, the adhesion tension; S_2, the surface tension of the liquid; K, the adhesion constant; and $-Q$, the heat of wetting. This equation can be simplified if, instead of the adhesion tension, we use the equivalent value KS_2. We then have the expression:

$$-Q = a(KS_2 - KT \; dS_2/dT)$$

But

$$S_2 - T \; dS_2/dT = E_2, \text{ the total surface}$$

energy of the liquid and it must follow that:

$$-Q = aKE_2.$$

Thus, given the specific surface area of a sample of silica and the adhesion tension (or adhesion constant) of a liquid for the silica it is possible to calculate the heat of wetting of the solid (per gram) by the liquid.

In deriving the above equation three assumptions were implied or stated and it is now desirable that their soundness be considered. It was necessary, first, to assume that silica gel presents the same type of surface to the wetting liquid as does the mineral silica used in determining the adhesion tensions. While this point is not susceptible of direct proof the silica used in each case was of a high degree of purity and, since no reason can be advanced for believing the surface energy relations of the two silicas to be different we feel justified in proceeding under the assumption that they are the same.

A second assumption was implied in the entire derivation—namely that data obtained from the displacement pressures set up at a liquid-liquid interface in pores of silica could be compared to energy changes when silica is immersed in pure liquids. In the adhesion tension determinations it was necessary to measure the equilibrium pressure set up by a liquid-liquid interface in capillary pores of the solid and there is a possibility that mutual saturation of water and organic liquid occurs, thus causing the measured values to represent the free energy changes when saturated liquids wet the solid. Evidence that any error due to such a cause is negligible is found in the following: Bartell and Whitney (results not yet published) have called attention to the fact that the work of adhesion between silica and an organic liquid is approximately 1.10

[1] Harkins and Dahlstrom: loc. cit.
[2] Bartell and Hershberger: Ind. Eng. Chem., **22**, 1304 (1930).

times the work of adhesion between water and the same organic liquid and that this ratio is constant for a great many liquids. In calculating the work of adhesion between a solid and a liquid it was necessary to use the value of the adhesion tension of the liquid against the solid. If mutual saturation influences the determined values of the adhesion tensions the effect should be confined to the values for liquids which form a zero contact angle with the solid, since the determination of the adhesion tension of a liquid which forms a finite angle with the solid requires only the measurement of the pressure with which the liquid displaces air from the pores and at no time is a liquid-liquid interface used. Such a determination should be free from any error due to mutual saturation. It was found, however, that the work of adhesion ratios calculated as above for contact angle liquids agreed with the ratios found for zero contact angle liquids. Consequently it would seem that any error due to mutual saturation in the displacement pressure cells is very probably smaller than the error of the experiment.

Finally, besides the fundamental assumptions just discussed, a third assumption was necessary to transform the equation into a usable form. Thermodynamically, the development was rigorous to the point that:

$$-Q = a(A_{12} - T \, dA_{12}/dT)$$

Experimental data concerning the temperature coefficient of adhesion tension, dA_{12}/dT, are not available as yet but the equation was changed by Bartell and Fu into a form of which all the terms except area are known by substituting $K \, dS_2/dT$ for dA_{12}/dT. The substitution follows from the fact that:

$$A_{12} = S_1 - S_{12} = KS_2,$$

and therefore:

$$dA_{12}/dT = K \, dS_2/dT.$$

This expression is based on the assumption that K is independent of temperature, an assumption which the authors in their preliminary paper did not justify further than to state that the error so introduced, if any, must be very small. It is, however, possible to justify the assumption in a qualitative way and even to estimate the order of magnitude of the error that may be introduced thereby. At $25°C$. A_{12} is K times as large as S_2 and at the critical temperature both A_{12} and S_2 become zero. It is known that the surface tension of liquids decreases in an *approximately* linear fashion as the temperature increases. Adhesion tension, measuring the decrease in free surface energy when a solid is wet by a liquid is principally dependent upon the adsorption of liquid molecules upon the solid, and such adsorption has been shown to decrease in an *approximately* linear fashion with temperature. Since both S_2 and A_{12} decrease toward the same point in an *approximately* linear manner, and since at $25°C$. $A_{12} = KS_2$, it follows that at any other temperature A_{12} must be K times as large as S_2, or, in other words, K does not vary with changing temperature.

In this justification, however, two approximations were involved and it is important that we attempt to evaluate the probable error introduced thereby.

While it is true that over short ranges of temperature dS_2/dT is practically constant, the line defined by this slope will not cross the surface tension axis of coordinates at the critical temperature. In Table VIII are shown, in the first column, values for the temperature coefficient of surface tension (dS_2/dT) taken from the literature. In the second column are shown the temperature coefficients that would be observed if the surface tension of each liquid decreased in an exactly linear fashion from its value at 25°C. to zero at its critical temperature. It is seen (column 4) that the difference between the two sets of values is not less than 19 per cent for any of the liquids and is as high as 35 per

TABLE VIII

Comparison of dS_2/dT with $S/(t_c-25)$ at 25°C

Liquid	$-dS_2/dT$ (expt.)	$-S_2/(t_c-25)$	Difference	Per cent Difference
Water	.155	.206	.051	34
Benzene	.132	.107	.025	19
Chlorbenzene	.121	.098	.023	23
Ethyl benzene	.110	.088	.022	25
Chloroform	.137	.111	.026	19
Carbon tetra-chloride	.124	.101	.023	19
Hexane	.105	.085	.020	19

cent in the case of one of them (water). If, then, the adhesion tension of the liquid against silica should decrease in an exactly linear manner to zero at the critical temperature, the deviations of $K \, dS_2/dT$ from the true dA_{12}/dT would be between 20 and 35 per cent. Since, however, the evidence that A_{12} decreases linearly with temperature is of such a nature that it is possible to state only that the decrease is approximately linear and since there is nothing to indicate that any deviation from an exact linear relation is in one direction or in the other, the deviation of dA_{12}/dT from $K \, dS_2/dT$ may be either smaller or larger than the figures given above.

Thus there is introduced into the expression connecting adhesion tension and heat of wetting a term of considerable uncertainty which will tend to throw some doubt on the absolute correctness of values calculated by use of the expression. The relative values for different liquids, however, should be approximately correct, and we feel justified in comparing relative values of heats of wetting calculated from adhesion tension data by means of this expression with the relative values actually observed. In fact they are probably within the limits of error usually involved in heat of wetting determinations.

If benzene is again used as the reference liquid, as was done in calculating the values for Table V, it will be necessary to arbitrarily choose a value for a in the expression

$$-Q = aKE_2$$

that will make $-Q$ equal to unity. When this is done and the same value of a is used to calculate the heats of wetting of silica by the other liquids the values

obtained for the heats of wetting are those shown in the fourth column of Table IX. For purposes of comparison, the relative heats of wetting observed are recorded again in the fifth column of the same table. The substantial agreement between the two sets of values is satisfactory in view of the fact that in developing the equation for obtaining the calculated values it was necessary to resort to an assumption that invalidates the absolute accuracy of the results.

There is evidence to indicate that the absolute values, as well as the relative values for a series of liquids, of the heats of wetting calculated from adhesion tension data are approximately correct. The specific surface area of silica gel

<div align="center">

TABLE IX

Comparison of Observed and Calculated Values of Heats of Wetting

</div>

Liquid	K*	E_2	Relative values of		On basis of $a = 5 \times 10^6$	
			$-Q_{calc.}$	$-Q_{obs.}$	$-Q_A$[†]	$-Q_R$[‡]
H_2O	1.07	118.2	1.21	1.51	15.1	19.0
$C_6H_5NO_2$	1.33	79.4	1.01	1.21	12.6	15.2
C_6H_6	1.55	67.6	1.00	1.00	12.5	12.5
C_6H_5Cl	1.25	69.0	0.81	0.94	10.1	11.8
$C_6H_5C_2H_5$	1.45	61.4	0.85	0.85	10.6	10.6
CCl_4	1.39	63.4	0.77	0.69	9.6	8.5
C_6H_{14}	1.42	49.5	0.67	0.56	8.4	7.0

* K—values obtained from work of Bartell and Whitney (unpublished).

† $-Q_A$—calculated from adhesion tension data.

‡ $-Q_R$—calculated from relative values observed.

has been estimated by several investigators using different means and the values fall fairly close to 5×10^6 cm.² per gram as an average. The specific surface may vary between rather wide limits, depending upon the method of preparation and the activation treatment of the gel, but the average of the values for specific surface area as estimated by other authors should be the same as the area of some of the more highly activated gels used in the present work. The heats of wetting by the liquids in question of a gel whose specific surface area is taken arbitrarily as 5×10^6 cm.² per gram can be calculated from adhesion tension data. The values obtained by such calculation are those shown in the sixth column of Table IX. Comparison of these values with the actually obtained heats of wetting presented in Tables II, III, and VI shows at once that there can be obtained by calculation from adhesion tension data approximately correct values for heats of wetting and, therefore, for total energies of immersion. In the final column of Table IX we have shown heats of wetting by the same liquids (calculated from the observed relative heats of wetting) of an hypothetical gel whose heat of wetting by benzene coincides exactly with the calculated heat of wetting by benzene shown in the preceding column. These were included for purposes of comparison since there are not included in the previous tables, experimental values for heats of wetting of any

one sample of silica by all the liquids. It is obvious, of course, that the relative discrepancies between the figures of the last two columns are the same as those found between columns 4 and 5. Considering the nature of the calculations involved this agreement is satisfactory.

An objection has been made to the use of the displacement pressure method for measuring adhesion tensions on the ground that the solid when packed into the cell is exposed to the vapors of the liquid before wetting occurs with the result that what is measured is not the free energy of immersion of the solid surface itself in the liquid but the free energy change, which occurs when the solid coated with an adsorbed film of vapor is immersed in the liquid. Since, however, the total energy of immersion values calculated from adhesion tension data do agree so well with the values calculated from heats of wetting, it seems justifiable to conclude that the adhesion tensions so determined must represent closely the free energies of immersion of the dry powder in the liquid. That the heat of wetting represents the total energy of immersion of a solid in a liquid is also a justifiable conclusion.

Summary

1. Methods of determining the change in free surface energy when a solid-air interface is replaced by a liquid-air interface are briefly discussed.

2. A brief survey of the literature concerning attempts to relate heats of wetting to total surface energy changes is given.

3. It is found that the heats of wetting of one silica gel by a series of liquids stand in the same ratio to each other as the heats of wetting of any other other silica gel by the same liquids. This is found to be true for gels varying in method of preparation, in physical properties (such as hardness), in water content and in activity.

4. It is deduced from the above relation that, even though it is known that silica gel contains small amounts of water, the heats of wetting of a gel by a series of liquids have the same relative values as the total energies of immersion of *dry* silica in the same liquids.

5. The theoretical equation relating adhesion tension to heat of wetting is discussed with especial attention to the approximations involved and the probable extent of the errors introduced by using such approximations.

6. Relative heats of wetting calculated from adhesion tension data are compared with relative heats of wetting observed experimentally and satisfactory agreement obtained.

7. Absolute heats of wetting calculated from adhesion tension data, on the basis of an assumed area for the gel, are found to agree satisfactorily with the observed heats of wetting.

8. The above facts are used to substantiate the probable correctness of the adhesion tension values as determined by displacement pressure measurements and to indicate that adhesion tension and free energy of immersion are numerically the same.

University of Michigan,
Ann Arbor, Michigan.

HEATS OF FORMATION AND −M/N RATIOS

BY G. B. HEISIG

The number of molecules of different compounds which condense per ion pair formed (−M/N ratio) and their heats of formation, which may be obtained directly or by a simple calculation from data given in the International Critical Tables,[1] are given in Table I. These data show that the −M/N ratio is highest for those compounds having negative heats of formation from elements
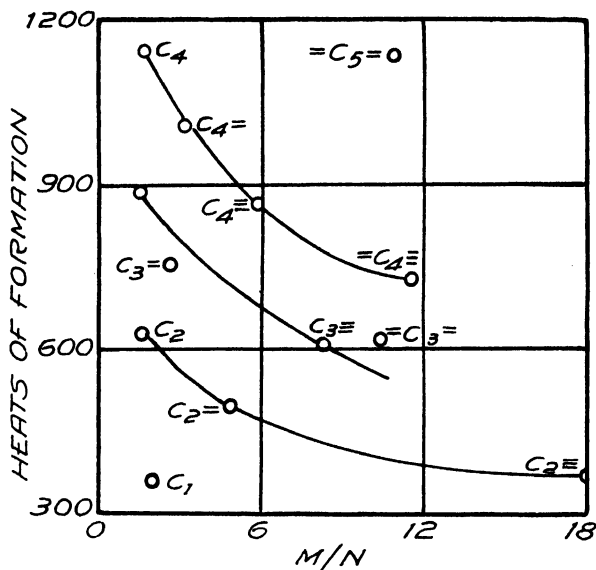
Fig. 1
Heats of Formation calculated from Fajans' Atomic Linkages and −M/N.

in standard states, and lowest for those having positive heats of formation. Since the heat of formation of many of the hydrocarbons whose polymerization by radon has been studied are not available, all were calculated by means of the atomic linkages of Fajans.[2]

The following values for the atomic linkages were used:

$$C - C \; 73.5 \text{ kg-cal.}; \; C = C \; 122.9 \text{ kg-cal.}$$
$$C \equiv C \; 161.6 \text{ kg-cal.}; \; C - H \; 92.4 \text{ kg-cal.}$$
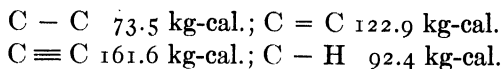
The calculated values agreed reasonably well with those obtained experimentally as can be seen in Tables I and II. The heats of formation of hydrocarbons when calculated from the combination of atoms are all positive.

[1] Inter. Crit. Tables, Vol. V, 163, 169-207 (1929).

[2] Fajans: Ber., 53, 643 (1920); 55, 2836 (1922); Z. physik. Chem., 99, 395 (1921); Taylor: "Treatise on Physical Chemistry," 323 (1931).

This is due to the high heat of dissociation of the hydrogen molecule—about 100 kg-cal—and the high heat of sublimation of carbon—147 kg.-cal. The values are given in column 2 of Table II. When these heats of formation are plotted against the $-M/N$ values there is no clear relation between them, as can be seen from Fig. 1. However, for a given number of carbon atoms the
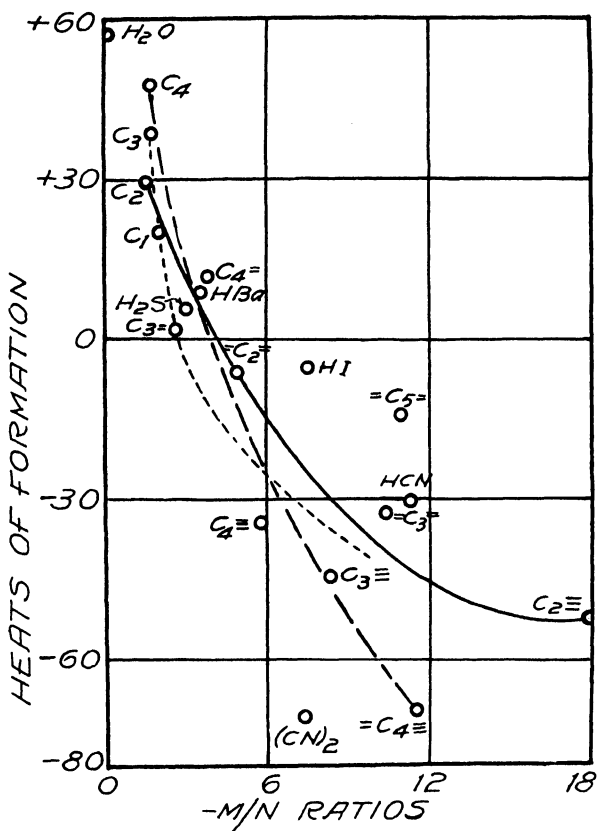
FIG. 2

Heats of Formation of Hydrocarbons from Diamond and H_2 (other cpds from atoms in standard states) and $-M/N$.

$-M/N$ ratio increases with the degree of unsaturation while the heat of formation decreases. The heats of formation from atoms were then converted to the heats of formation of the compounds from hydrogen and the diamond, using the values.

$$\text{C atom} \rightarrow \text{C diamond} + 149.3 \text{ kg-cal.}$$

$$H_2 \quad \rightarrow 2H \quad - 100. \text{ kg-cal.}$$
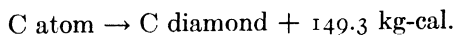
by the relation—

Heat of formation C_mH_{2n} from H_2 and diamond = Heat of formation C_mH_{2n} from atoms of carbon and hydrogen $- (n/2 \times 100) - (m\ 149.3)$.

TABLE I

−M/N and Heats of Formation from Elements

Compound	−M/N	Heat of Formation	
		Diamond + H_2[a]	From Elements in Standard States[b]
Methane[c]	2.2	20.4	19.1
Ethane	1.7	25.5	23.4
Propane	1.7	30.3	
Ethylene	5.1	− 6.4	− 9.6
Propylene	4.9	− 2.0	
Acetylene	20.0	−54.8	−54.3
Allylene[d]	8.3	−44.6	
Hydrogen Iodide (dec)	7–8		− 5.9
Hydrogen Bromide (dec)	3–4		8.7
Hydrocyanic Acid	11.3		−30.2
Cyanogen	7.4		−70.8
Water (dec)	.01		57.8
Hydrogen Sulfide (dec)	2.5–4		5.3

[a] Calculated from the data Int. Crit. Tables, **5**, 163.

[b] Int. Crit. Tables, **5**, 169-207.

[c] The hydrocarbons are indicated on Figs. 1 and 2 by the number of carbon atoms and the number of double and triple bonds thus $C_2 \equiv$ is acetylene, etc.

[d] Heisig, unpublished results.

TABLE II

−M/N and Heats of Formation

Compound	−M/N	Heats of Formation	
		From Fajans' Atomic linkages	From H_2 and Diamond[a]
Methane	2.0	369.6	20.3
Ethane	1.5	627.9	29.3
Propane	1.5	886.2	38.3
Butane	1.7	1144.5	47.3
Propylene[b]	4.9	750.8	2.9
Butylene	3.8	1009.1	11.9
Ethylene	4.8	492.5	− 6.1
Butine (sym)	5.8	863.0	−34.6
Propine	8.3	604.7	−43.2
Allene	10.4	615.0	−32.5
Isoprene	10.9	1132.0	−14.5
Vinylacetylene[b]	11.5	727.6	−69.6
Acetylene	18.0	346.4	−52.2

[a] Calculated from heats of formation obtained from Fajans' atomic linkages.

[b] Heisig, unpublished results.

The values obtained are given in column 3 of Table II. These values are plotted against the $-M/N$ of the compounds in Fig. 2. This plot shows clearly that the $-M/N$ ratios of those compounds whose heat of formation is positive or a small negative value, is very close to 2. The M/N ratios of the compounds whose heat of formation is negative increased, as a rule, with an increase in the negative heat of formation of the compound. This indicates that some of the energy stored in the molecules of these substances is used during the polymerization of the hydrocarbon. The $-M/N$ ratio then, would be dependent on the energy received from the α-particle and that available from the polymerization of the substance.

Lind and Bardwell[1] state that the composition of the liquid formed in the polymerization of methane, ethane, propane, or butane – –whose compositions are expressed by the formula C_nH_{2n+2} – – is C_nH_{2n}. The $-M/N$ for these hydrocarbons is very nearly 2, and if the average molecular weight of the product were known, the energy change in the process could be readily calculated by Fajans' atomic linkages. However, a calculation can be made which will show whether the process is endo- or exothermal in the following way:

If y is the $-M/N$ ratio, and x is the number of ion pairs involved in producing a molecule of condensate, then xy molecules of the saturated hydrocarbon C_nH_{2n+2} will form a molecule of the condensate, whose composition and molecular weight will be $C_{xyn}H_{2xyn}$. Such a molecule can be built up by assuming the formation of an ethylene derivative by the condensation of two molecules of the original hydrocarbon, and the addition of x simple aggregations at the double bond. Thus for the case of $x = 3$:

$$\begin{array}{ccccccc} & H & H & & H & H & & H\ H\ R\ H\ R & H \\ 2RCH_3 \rightarrow & RC & = & CR & \text{and } 3RC & = & CR \rightarrow & RC\text{-}C\text{-}C\text{-}C\text{-}C & = & CR \\ & & & & & & & H\ R\ H\ R \end{array}$$
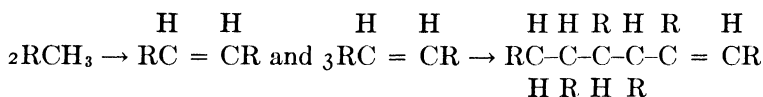
With these assumptions in mind we can now show that for the condensation of xy molecules of C_nH_{2n+2} to form $C_{xyn}H_{2xyn}$, energy is required. There are xyC_{n-1} single bonds in xy molecules of the saturated hydrocarbon, and $C(xyn-2)$ single bonds in the product, hence $(xy-2) \times 73.5$ kg-cal. are available as a result of the increase in the C–C bonds. A double bond has been formed, and 122.9 additional calories are available to partially balance the energy required in the condensation process. There are $xy \times H_{2n+2}$ carbon-hydrogen bonds in the original hydrocarbon and only H_{2xyn} in the condensate, thus making $2xy \times 92.4$ kg. cal. required to break the carbon-hydrogen bonds. To offset the $2xy \times 92.4$ cal. required to break the C–H bonds, 122.9 calories are available through the formation of a double bond and an additional $(xy-2) \times 73.5$ cal. from the formation of $(xy-2)$ C–C bonds. That is—

$C_{xyn-xy} \times 73.5 + H_{2xyn+2xy} \times 92.4 \rightarrow 122.9 + C_{xyn-2} \times 73.5 + H_{2xyn} \times 92.4$ and $xyC_n H_{2n+2} \rightarrow C_{xyn} H_{2xyn} - (111.3\ xy + 24.1)$ cal.

From the equation the energy required to convert xyC_nH_{2n+2} to $C_{xyn}H_{2xyn}$ is

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[1] Lind and Bardwell: J. Am. Chem. Soc., **48**, 2345 (1926).

($111.3xy + 24.1$) cal. The polymerization, then is *endothermal*, and therefore is probably not a chain reaction.

In another paper by Lind, Bardwell and Perry[1] the empirical formula of the condensate from ethylene is approximately C_nH_{2n} and the formulas of the condensates of propylene and butylene are also represented by this general formula. Hence the change is:

$$xyC_nH_{2n} \rightarrow C_{xy}H_{2xyn}$$
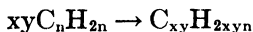
Using the same method of approach one obtains the net energy change for ethylene and its homologs from the equation:

$$xy(129.9 + C_{n-2} \times 73.5 + H_{2n} \times 92.4) \rightarrow 122.9 + C_{xyn-2} \times 73.5 \times H_{2xyn} \times$$
92.4 and $xyC_nH_{2n} \rightarrow C_{xyn} H_{2xyn} + (24.1\ xy + 24.1)$ cal.
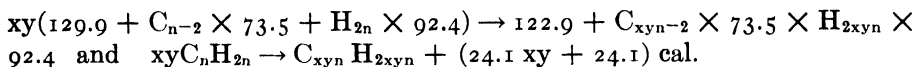
Therefore, in forming a molecule of the condensate ($24.1\ xy + 24.1$) cal. of heat *become available* in addition to the energy supplied by the alpha-particle. The reaction, unlike that of the saturated hydrocarbons, is *exothermal*.

The polymerization of acetylene, methylacetylene and dimethylacetylene takes place with but little evolution of hydrogen and methane. The action may be represented[2] by the equation: $xy(C_nH_{2n-2}) \rightarrow C_{xyn} H_{2xyn-2xy}$ and the energy change involved is given by

$$161\ xy + C_{(xyn-2xy)} \times 73.5 + H_{(2xyn-2xy)} \times 92.4 \rightarrow xy \times 122.9 + xy \times$$
$73.5 + H_{(2xyn-2xy)} \times 92.4 + C_{(xyn-2xy)} \times 73.5$ and $xyC_n H_{2n-2} \rightarrow C_{xyn}$
$H_{2xyn-2xy} + (34.8\ xy)$ cal.
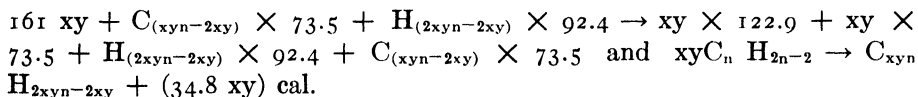
Thus $34.8\ xy$ cal. *are liberated* making the condensation process of the acetylenes *exothermal*.

The energy involved in the polymerization of vinylacetylene, and allene has also been calculated. In the case of the first compound, it is assumed that addition occurs at the triple bond. From xy molecules of this hydrocarbon, xy triple bonds must be broken requiring xy 161.6 cal. and a double and single bond will be formed releasing xy $\times$ 73.5 and xy $\times$ 122.9 cal. respectively. There will then be released xy $\times$ 34.8 cal. in this exothermal process. The assumption is made in the case of allene that addition occurs at a double bond. When xy molecules condense xy double bonds are broken, and 2 xy single bonds are formed, making xy $\times$ 24.1 cal. available.

The $-M/N$ ratio of the saturated hydrocarbons is about 2, while those of the unsaturated hydrocarbons is larger. This leads to the suggestion that the energy resulting from the condensation process is a contributing factor in determining the value of the $-M/N$ ratio. The reason then that the unsaturated compounds have a higher $-M/N$ value is due, in part at least, to the energy released in the condensation process which is available in addition to the energy imparted by the α-particle. In the case of the saturated hydro-

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[1] Lind, Bardwell and Perry: J. Am. Chem. Soc., **48**, 1556-75 (1926).

[2] Since but little is known of the structure of the polymer of acetylene formed (cuprene), and nothing concerning the structure of the condensates from methyl and dimethylacetylene, it is assumed for purposes of calculation, that there are an equal number of single and double bonds in the product.

carbons, only the energy of the α-particle is used in the process. The heats of formation of the hydrocarbons thus may be used as a basis for predicting the approximate magnitude of the $-M/N$ ratios. This value has not been determined for cyclopropane. Cyclopropane has a heat of formation of -8.5 kg-cal. and if this relation holds for cyclic derivatives its $-M/N$ ratio therefore should be somewhat larger than that of propylene which has a heat of formation of -2.0 kg-cal. and a $-M/N$ of 4.9.

Hydrocarbons are also polymerized by an electrical discharge. Lind and Glockler[1] have shown that the pressure change as a function of time, the average composition of the liquid condensate, etc., are the same as that observed with radon hence the heats of formation have a similar influence in both methods of producing polymerization.

Summary

1. The condensation of the saturated hydrocarbons is endothermal and the $-M/N$ values are small.

2. The condensation of unsaturated hydrocarbons is exothermal and their $-M/N$ values vary in general, with their negative heats of formations from elements in their standard states.

3. The greater the negative heat of formation of substances other than hydrocarbons, the greater is the $-M/N$ ratio.

4. The heats of formation from the elements in their standard states may be used to predict approximate $-M/N$ ratios.

November, 1931,
Minneapolis, Minn.

[1] Lind and Glockler: J. Am. Chem. Soc., **52**, 4450-61 (1930).

A STUDY OF THE STRUCTURE OF
ELECTRODEPOSITED METALS
PART I

BY L. B. HUNT

The purpose of this paper is to present a critical review of the state of our knowledge of the factors which influence the structure of electrodeposited metals, and to put forward a working hypothesis to account for the observed variations in structure with differing conditions of deposition and amongst the various metals and their salts. A number of theoretical views on this subject have been advanced from time to time, but although the majority of them undoubtedly represent partially the actual state of affairs, none of them has been found to account satisfactorily for all the phenomena. It might be thought that to add one more to these hypotheses would be merely to labour the point unduly, but it is submitted that the views to be advanced are more in line with modern ideas on the conditions in electrolytic solutions and in metallic crystals than any of the previously outlined theories. Up to the present no attempt has been made to apply these recent views on interionic forces, ionic solvation, origin of potential and crystal structure to the study of electrodeposition, and the present paper is designed to point the way to a more complete correlation of the accumulated data on electrodeposition with these newer conceptions. It is as a result of the incorporation of these theoretical views that a new working hypothesis has been evolved to fit the facts of the case. Even if it is eventually discarded, a working hypothesis serves its purpose if it has suggested a new classification of known phenomena, or a recognition of the sequence and inter-relatedness of the facts, and for these reasons the writer's views are now presented for criticism.

The Mechanism of Deposition

It will first of all be necessary to consider the precise manner in which a positively charged metal ion on reaching the cathode, becomes transformed into an "atom" of solid metal and takes its place in the crystal lattice. The views which have been advanced on this point fall naturally into two divisions —those postulating one instantaneous process of ion discharge and crystallisation, and those based on the conception of an intermediate state in which the ion or atom exists just prior to entry into the lattice. The essential differences between the type of crystallisation under discussion and those types more commonly met with should here be pointed out. The crystallisation of a metal from the molten state bears practically no resemblance to electrodeposition, in that the distribution in the first case is virtually unaltered, whilst in deposition the distribution in the two phases is widely different. This point is brought out by the important part played by diffusion in affect-

ing the structure of electrodeposits. Further, the formation of crystals of an inorganic salt or an organic compound from solution will not permit of comparisons being made, in so far as the speed of deposition is governed by a definite driving force in the form of the current, or, in other words, the supply of electrons, whereas the speed of crystallisation of a salt or other compound is dependent on supersaturation, which again is influenced by a number of factors. Another type of crystallisation which has recently received attention is the formation of metal films from the vapour phase, but here again comparisons are invidious owing to the absence of solvent. The nearest approach to the process of crystallisation with which we are dealing is to be found in the electrolysis of fused salts, and although the absence of solvent destroys the analogy, a certain amount of helpful information may be obtained from a study of this process. The chief reason for making these distinctions is that several writers, notably Hughes,[1] acting on a suggestion made by Lehmann,[2] have developed their views on the structure of electrodeposited metals by assuming an analogy with other forms of crystallisation. The former author conceives a "metal atom concentration" at the cathode surface, and one is then asked to imagine a state of greater or less supersaturation in this layer of metal atoms. If supersaturation is great, rapid deposition of small crystals will result, as is the case with the crystallisation of a salt from solution. It is therefore necessary to assume that electrons enter a short distance into the solution to form metal atoms, and that these uncharged atoms then proceed in some way to the charged cathode, to form crystals the size of which is to be governed by the concentration of the atoms. The writer is not aware of any evidence on which these two assumptions can be justified. Aten and Boerlaage[3] had previously put forward similar views with regard to the formation of metal atoms at a short distance from the cathode, and subsequent crystallisation from the resulting supersaturated solution, but they had also taken into account another factor, the change of polarisation with current density. Blum and Rawdon[4] then proposed their theory connecting the structure of electrodeposited metals with the cathodic polarisation during deposition, in which they assumed that ion discharge and metal crystallisation constitute one and the same process, an ion being discharged at a point on the cathode surface at which the lowest discharge potential is required. The implications of the latter conception will be discussed in detail later in the paper. Frölich and Clark[5] are also of the opinion that there is no intermediate stage in electrodeposition and that a single instantaneous process occurs.

Two other views which have been put forward with particular reference to the iron group metals must be mentioned. Kohlschütter[6] and his coworkers suggest that the discharged metal atoms remain in a dispersed state in a film of hydrogen for some finite period, after which they orient themselves to form crystalline structures. Glasstone[7] has advanced the view that the metal (nickel in particular) may be deposited in a labile state, due to the two electrons entering the 4-quantum orbit. This metastable form would then be transformed at a definite rate into the ordinary metal.

In 1928 Volmer[8] published an important paper, which has received little, if any, attention in this country, in which he suggested that deposition takes place by layers of atoms. Until a given layer is complete a certain proportion of the ions will find themselves in an intermediate state, between that of the original solution and that which they will eventually take up in the lattice. The observed polarisation phenomena are attributed to this retardation effect. Brandes[9] has further developed this view by assuming that an ion on entering the Helmholtz double layer will be deprived of its water envelope and will then seek out a convenient place on the lattice. The double layer will constitute a condenser, the potential difference in which will be proportional to the quantity of electricity brought up. The more easily an ion can find a suitable place for discharge the less will be the charge in the double layer, and hence the less the polarisation.

These two suggestions thus appear to fall into the "instantaneous process" class, although including the idea of some delay just prior to discharge. Present ideas on the phenomenon of ion discharge in general, and on the ionic nature of crystals would appear to support the conception of a single process of discharge and entry into the lattice. Further, the electrostatic attraction between cathode and cation will increase rapidly as the distance separating them decreases, so that any pause in the progress of the ion is difficult to imagine. Nevertheless, the existence of a double layer of dehydrated ions which are constantly being discharged and replaced cannot be ignored.

Nucleus Formation

On entering the field of the crystal lattice, the ionic atmosphere will be repelled—pushed to the rear of the approaching ion, and ultimately broken away. What will then prevent the ion from taking its place in an existing lattice, i.e. what will cause it to form the nucleus of another lattice? The possibilities are two in number. Either the formation of some kind of two-dimensional lattice, having a different orientation, immediately before discharge, according to Volmer's interpretation of the state of affairs, may lead to nucleus formation, or alternatively it may be supposed that during the time interval preceding the arrival of the ion, and after the arrival of the previous ion, some other body shall have come to rest at this point on the lattice. It is conceivable that some of the water dipoles which are continually being brought up by the ions may remain attached to the lattice, having their negative poles towards the positive ions in the lattice. In this case further deposition would take place around and over the dipoles, with a consequent discontinuity in the lattice. A similar effect may be caused by particles of a colloidal nature which have migrated electrophoretically into the cathode layer, or even by undissociated molecules forming dipoles attached to the crystal lattice. Although this process is by no means unlikely, the frequency of its occurrence is probably quite small, depending on the interval between the arrival of ions at a given point on the lattice, and thus on the current density.

The conception of a two-dimensional lattice has been successfully applied by Volmer[10] to the case of metallic films formed from a stream of vaporized metal particles, and there is a certain amount of experimental evidence which might be used to support a similar conception in the case of electro-deposition. A periodicity has frequently been observed during deposition, particularly from complex cyanide solutions, and deposits prepared in the presence of gelatin have been found by Grube and Reuss[11] to consist of alternate layers rich in copper and gelatin respectively. Hoekstra[12] has recently concluded that deposition occurs for most metals in films of approximately one thousand atoms in thickness. Any "two dimensional lattice" formed in this way will probably consist of dehydrated ions prior to discharge, as suggested by Volmer and Brandes. Even in this case, however, there will exist a strong tendency for the layer to follow the orientation of the surface layer of the cathode, and so to continue the crystal structure. Thus some sort of interference with crystal growth due to the inclusion of an electrolytically inert body is most likely as a cause of nucleus formation.

Crystal Growth

In the cases of crystallisation from the molten state or from solution, crystal growth can take place, once a nucleus has been formed, in all directions, or rather in all three planes. With electrodeposition, however, growth is largely confined to a plane normal to the cathode, but may also take place to a limited extent in a plane parallel to the cathode. The writer considers that it is necessary in discussing crystal growth of electrodeposited metals to differentiate these two forms of growth. In the case of growth parallel to the cathode plane, everything will depend upon the structure of the cathode surface and the behaviour of the initial lattice layers. It has been pointed out first by Huntington[13] in 1905 and afterwards by Blum and Rawdon[14] in 1923, that if a cathode is suitably etched in order to expose the normal structure (as distinct from the polished broken-down surface layer) it is possible to obtain an electrodeposit which will consist of continuations of the existing crystals in the cathode. In other words, deposition may take place entirely by crystal growth and with no nucleus formation whatever. The writer has found it necessary in preparing deposits of this type, to employ fairly high temperatures and low current densities; that is, to maintain a plentiful supply of metal ions to the cathode. It is apparent that, given a suitable metal ion supply, cathode structure will have a predominant affect in the growth of the deposit, and nucleus formation may be absent. If, however, the cathode structure is not favourable to reproduction, but the metal ion supply is well maintained, a fibrous type of structure will result due to growth taking place in a normal plane but not in a parallel plane. On the other hand, if the metal ion supply is at all restricted, nucleus formation will be pronounced whatever the cathode structure.

That growth in a normal plane actually takes place by layers is now fairly well established. Hedges[15] has recorded a periodicity in the deposition of

cadmium from potassium cyanide solutions, which he attributed to secondary reaction. It is very doubtful, however, if secondary reaction is present in electrodeposition (cf. Glasstone[16]) and a more feasible explanation of this rhythmic effect would seem to be the alternate supply by diffusion of the two types of cations—metal ions and either hydrogen or alkali metal ions. The writer has found in preliminary experiments that as the temperature is increased, periodicity becomes much less marked, and finally almost disappears. Hedges also found that the period increased with rise of current density. It seems probable, therefore, that the periodicity is due to two alternating processes, first the deposition of metal ions, leaving a cathode film depleted of these ions, followed by discharge of hydrogen ions. The upward movement of the discharged hydrogen will promote diffusion of further metal ions, and the cycle will be repeated. Periodicity is known to be favoured by the presence of colloidal matter, which may cause the isolation of the growing crystal from the supply of metal ions, as apparently occurred in the experiments of Grube and Reuss.[11]

Crystal Orientation

Several workers have recently applied the methods of X-ray analysis to the determination of orientation in electrodeposited metals. Frölich and Clark[17] studied deposits of nickel and concluded that low current density and high temperature gave the best development of structure. Hydrogen evolution was found to hinder the regular arrangement of the crystals. Frölich, Clark and Aborn[18] later studied lead deposits prepared from a number of electrolytes. The deposit from a perchlorate solution containing gelatin and excess acid was found to give minimum grain size, freedom from dendrites, and considerable evidence of preferred orientation. Whereas the grain size decreased as usual with rise of current density, preferred orientation was found to increase, in contradistinction to the results obtained with nickel. Bozorth[19] found that deposits of copper, zinc and cadmium had their crystals oriented at random, whilst iron, nickel and cobalt showed special orientation. Bozorth suggested that orientation was associated with strain due to the codeposition of hydrogen.

Hirata and his co-workers[20,21] have examined deposits of silver, antimony, bismuth and tin, for orientation by means of X-ray analysis. Silver deposits from silver nitrate solutions were found to have the diagonal axes of the cubic crystals arranged parallel to each other along the axes of the fibrous material deposited. The microcrystals of bismuth were found to be arranged more regularly, the smaller the current density, and the concentration of electrolyte. When both current density and concentration were very small, crystals of considerable size were formed, having all their axes coincident. Similar results were obtained with antimony and tin. The data on this point will clearly not yet permit of generalisations being made. Certain results are contradictory, but the fact emerges that preferred orientation is generally favoured by slow deposition from dilute solutions. The significance of this result will be further examined in the latter portion of the paper.

The Nature of the Crystal Boundaries

An interesting speculation which arises here concerns the nature of the intercrystalline boundary. According to the view put forward by Bengough[22] and by Rosenhain and Ewen,[23] the interstitial spaces between adjacent crystals of a metal are filled by an amorphous film or layer. It is assumed that owing to the opposing tendencies of the crystalline forces at the frontier of two crystals, a certain number of metal atoms will remain in the irregular arrangement characteristic of the liquid state, so acting as an intercrystalline cement. These layers of amorphous or undercooled liquid metal are conceived to be formed during the process of crystallisation from the molten state, but it is difficult to imagine the production of amorphous material by the slow and ordered process of electrodeposition, in which the deposited ions will have ample time in which to arrange themselves in positions of minimum free energy. But crystals of cast and rolled metal can be caused to grow in the manner described above simply by the deposition of further metal, and no differences can be detected between the two parts of a crystal produced in this way. In this particular case non-metallic inclusions are almost certainly absent, and the best explanation would appear to be that suggested by Gough,[24] of an intercrystalline zone occupied by a large number of very small crystallites, the orientation of adjacent crystallites being slightly different, so that the change of direction from crystal to crystal is achieved by an integration of small changes.

In more normal cases when nucleus formation is prominent, the intercrystalline boundaries must necessarily contain the various inclusions which enter the deposit, and conditions approximate more nearly to the views of Tammann,[25] who imagines the boundaries in cast metals to consist of impurities. The results of Hirata show that nucleus formation may occur without change of direction in a normal plane. Whilst it would be expected that inclusions would generally occur in planes parallel to the cathode, Kistiakovski and his co-workers[26] have recently reported finding cuprous oxide in copper deposits in a plane normal to the cathode.

A curious feature of electrodeposition is the occasional production of isolated crystals or aggregates. This is usually met with in the cases of the heavy metals, although Hori[27] has recently published an interesting photograph of isolated copper crystals deposited on a single crystal of bismuth. Asahara and Sasahara[25] have obtained beautiful single crystals of thallium unbounded on all sides, from solutions of thallous sulphate. However, this question of boundary material is much too obscure for further discussion to be profitable. The point has been raised merely as a speculation.

The Relation between Structure and Cathode Polarisation

The theory proposed by Blum and Rawdon[4] in 1923 may be said to hold the field today as a working hypothesis. Although various discrepancies between experimental observations and the results expected from the theory have been recorded by Graham,[29] Macnaughton and Hothersall,[30] and by

Glasstone and Saniger,[31,32] it has not as yet been subjected to a theoretical criticism. It may be said at the outset that this hypothesis gives in general some indication of what is likely to result from a change in the conditions of deposition, and thus is of value in predicting alterations in structure. Decrease in grain size is in most cases actually accompanied by an increase in cathodic polarisation, but it is submitted by the present writer that polarisation is to be regarded more as a parallel result of certain other operative factors than as the first cause of decrease in grain size. The main idea of their theory is stated by Blum and Rawdon as follows:

"The forces which cause the atomic orientation or crystalline structure must be attractive, and must therefore counteract the tendency of the metal atoms to pass into solution as metal ions. In consequence the solution pressure of a metal crystal must be less than that of a single metal atom."

It is then assumed that the only solution pressure and corresponding normal single potential of any element which is characteristic and constant is that of the hypothetical single unoriented atom, or of a mass of metal, consisting of unoriented atoms. In support of this contention it is stated that the single potential of a metal varies with the state of division, being most negative for the finest state. Therefore, it is argued, a higher potential will be required to start a nucleus than to continue the growth of an existing crystal, and thus all factors which tend to increase the potential difference between cathode and solution will foster the formation of nuclei.

Now in the first place the statement that "the forces which cause the atomic orientation or crystalline structure must be attractive" deliberately ignores the existence of the repulsive forces which must of necessity balance the attractive forces in any solid body. Tomlinson[33] has recently shown that the repulsion is, in fact, the dominating factor in determining the properties of solids.

Further, an examination of the evidence submitted in support of the statement that the single potential of a metal varies with its state of division, discloses a misconception of the facts. The results of Lewis and Lacey[34] with copper electrodes are cited. These workers found that spongy copper electrodes varied amongst themselves by amounts of the order of 0.0003 volt, whilst coherent deposits might vary by as much as 0.01 volt. Three years later, however, Lewis and Brighton[35] found that sticks of lead scraped with a glass edge gave the same potential as lead deposited by electrolysis, either on lead or platinum, from lead perchlorate solutions. The average deviation was less than 0.0001 volt, and it was concluded that the lack of reproducibility in electrodes of solid metal is due solely to conditions of strain in the solid surface.

Reference is also made by Blum and Rawdon to Förster's "Elektrochemie wässeriger Lösungen" (1922 edition). In a footnote on page 181 Förster states that the metals nickel, cobalt, and iron, in the finely divided state, possess higher potentials than in the compact state, as wire or foil, and gives as his authorities Schoch,[36] Richards and Behr,[37] Schweitzer[38] and Schildbach.[39] All these workers compared the potentials of nickel, cobalt and iron

in the finely divided porous state, and in the solid state, and found that the finely divided metals gave potentials greater by about 0.03 volt. Schoch however came to the conclusion that the discrepancies were due to occluded hydrogen, and Schildbach found that by charging cobalt powder with hydrogen, potentials could be obtained which were still more negative.

On the other hand, Anderson[40] has recently investigated the electromotive behaviour of single crystals of zinc, and has found that the potentials of large single crystals were "very nearly equal, if not identical to" those of the electrodeposited metal. Straumanis[41] has also recorded identical potentials for single crystals and polycrystalline aggregates of zinc.

Now it is not contended that the potential of a finely divided metal may not differ from that of the same metal in a more compact form, in much the same way that the vapour pressure of a liquid varies with the size of the drops, but it is contended that the analogy is wrongly applied to the case of electrodeposition. In all cases (with the exception of abnormal spongy deposits) compact metal is under consideration, which is being built up gradually from identical crystal units, regardless of the ultimate size of the crystals, and it is submitted that the electrode potential of this metal will not vary with differing grain size. (It is necessary to avoid confusing "fine grained" solid metal with "finely divided" porous metal). The state of our knowledge on the origin and seat of potential is decidedly controversial and uncertain, but it is known that potential difference is a surface phenomenon, dependent on the thermionic work function of the metal, the free energy of solvation of its ions, and the concentration of ions in the cathode film, and not on any solution pressure of the metal. In effect then, it is submitted that the basic conceptions of the theory of Blum and Rawdon are untenable. The reason that a certain parallelism exists between their theory and the observed phenomena is to be found in the fact that polarisation is dependent on the compensating processes operating to supply metal ions to the cathode film.

Development of a Working Hypothesis

It is now proposed to evolve a working hypothesis to account for the variations in the structure of electrodeposited metals by a study of the contents of the cathode film, or diffusion layer, in the light of the most recent views on the behaviour of ions in solution. By making a general survey of the behaviour of most of the metals which are capable of being deposited, certain generalisations may be deduced with regard to the predominating influences which govern the crystalline form of deposited metals. Before actually dealing with conditions in the cathode layer, however, it will be necessary to consider the state of affairs in the bulk of the solution. The solutions normally employed for electrodeposition are necessarily concentrated and often very complex, and the work which has been carried out on the theory of solution cannot be extended to these solutions as yet. For simplicity a solution will first be considered which contains only one simple salt of the metal to be deposited. This salt will, of course, dissociate to some extent into cations and anions, both of which will in all probability be

hydrated. The remaining portion of the salt will remain as undissociated molecules, although complex ions may be formed by combination with the simple ions.

The Extent of Dissociation of Electrolytes

Our ideas on the subject of the degree of dissociation of salts in water and other solvents have undergone considerable change during the last few years, but no attempt has so far been made to apply the more recent views to the study of electrodeposition. Since the enunciation in 1923 of Debye and Hückel's theory[42] of complete dissociation and interionic forces, and the consequent turning of opinion away from the views of Arrhenius, it has become apparent that the two ideas are not diametrically opposed, but should rather be considered as complementary. The evidence for the existence in solution of undissociated molecules has gained more and more weight, due largely to the work of Fajans,[43] Davies[44] and their co-workers. By making certain simplifying assumptions, it has only recently become possible to calculate tentative values for the true degree of dissociation of a salt, and although the values obtained are in general considerably greater than those given by the conductance ratio, they none the less indicate that dissociation is far from being complete. Certain generalisations have been made by Davies as a result of several series of experiments.[45] Uni-univalent salts are in general found to be almost completely dissociated in water, bi-bivalent salts are practically all weak, whilst uni-bivalent salts occupy an intermediate position. The last named type of salts has recently been found to give somewhat anomalous results, varying from almost complete dissociation in the case of calcium chloride, down to considerable association with cadmium chloride.

The interionic forces will vary with the charge on an ion, the distance separating it from oppositely charged ions, the size of the ion, and its electronic arrangement. Thus univalent ions will tend to be dissociated to a greater extent than will bivalent ions whilst the highly localised positive field on a small ion having a structure remote from the inert gas type will tend to cause deformation of the anion and so promote association. This effect will be greater the larger the anion and the higher the valency of either ion. The co-ordinating tendency of the anion will also have an effect in depressing dissociation. Solvation will reduce the effects of the positive charge on the surface of a cation, and so tend to increase dissociation. Ives and Riley[46] state that when the co-ordinating tendency of the anion is sufficiently great to break down the solvated ion system the effect of the localised charge reaches its maximum and feeble dissociation results. Koch[47] has shown that it is necessary to assume that the solvent molecules exert an attractive force on the ions, and that these forces are specific for any ion and solvent. He has further shown that dissociation must in general be of a complex nature. The metal ion may appear alone, together with complex anions, or it may be practically confined to complex cations, depending on the relative affinities of anion and cation for the solvent.

The Behaviour of Ions in Solution

In order to obtain a mental picture of the process of electrodeposition, therefore, it is necessary to revise our ideas on the behaviour of ions in solution. Ions must no longer be considered as independent entities, but as closely connected bodies having mutually operative forces acting upon them. The foundation of the Debye-Hückel analysis is the conception of the unequal distribution of the ions owing to the interionic forces. The attractive force between cations and anions will tend to bring them into closer proximity whilst the repulsive force between like ions will tend to remove them. Thus any given ions will be surrounded by more unlike than like ions. This ionic "atmosphere" must necessarily bear an equal and opposite charge to the central ion. On the application of an E.M.F. the ion and its atmosphere will be impelled in opposite directions by the current, and the atmosphere must be continually building up in front of an ion and falling off in the rear. Thus a retarding influence is exerted on an ion in its movement towards an electrode, and metal ions must be removed against this retarding force in order to enter the crystal lattice on deposition. In all probability, therefore, the polarisation accompanying deposition is bound up with this resistance offered to the process by the interionic forces.

After the removal of a metal ion from its atmosphere there still remains the solvent envelope, which must be dissipated before entry into the lattice can take place. If as has been suggested above, dipoles may occasionally remain attached to the metal ion after its arrival on the cathode, interference with crystal growth will result, with the consequent formation of a nucleus.

Contents of the Cathode Layer

The composition of the cathode film in the type of aqueous solution normally used for electrodeposition may now be considered. The following scheme represents the various ionic and molecular species, and the directions in which they are moving with respect to the cathode.

Approaching	At Random	Leaving
Metal ions	Undissociated	Anions
Other cations	molecules	Complex anions
(H; K; etc.)	Solvent-water	Water dipoles
Complex cations	molecules	
Water dipoles		
Colloidal bodies		

(It is assumed that the only colloidal particles which need be considered are those which migrate towards the cathode.)

The removal of metal ions from the cathode layer will be compensated by such processes as migration, diffusion, convection, and agitation, and at the critical current density an equilibrium will exist such that equal quantities of metal ions are deposited from the cathode film, and brought into it, in a given time. Below the critical current density the compensating processes

will be able to supply ions at the same speed as they are deposited, and thus the velocity of the compensating processes must increase with the velocity of deposition. Glasstone[48] has recently published a mathematical relationship connecting speed of diffusion, and limiting current density with the concentration of electrolyte.

Increase of temperature will increase the rates of diffusion and convection, and also reduce the thickness of the diffusion layer, so favouring the rapid attainment of equilibrium and increasing the limiting current density. Agitation will play a similar part to increase of temperature. The important factor in this cathode layer is of course the concentration of metal ions therein. This fact has been recognised by the previous workers in the subject, but the suggestions now to be put forward are based on the relation between this metal ion concentration and the concentration of the other ions and molecules in the cathode layer.

The Interference Theory

The hypothesis which is suggested by the writer may be briefly set out as follows:—

The crystalline structure of an electrodeposited metal will be governed by the relation of the metal in concentration in the cathode film to the concentration of the other constituents of that film. If the proportion of metal ions to inert particles is comparatively high, there will be little interference with crystal growth, and coarsely crystalline deposits will result. If, however, the proportion is low, due to low degree of dissociation, complex ion formation, high hydration of the metal ions, or the presence of colloidal matter that has migrated cataphoretically into the film, or has been joined therein, there will be considerable interference with crystal growth, with the consequent formation of many nuclei. Thus any change in the conditions of deposition which restricts the supply of metal ions to the cathode film whilst allowing that of the other particles to remain unaltered, will cause a diminution in the grain size of the deposit.

The mechanism of deposition according to this view will now be considered. A metal ion on approaching the cathode will seek to enter the lattice as soon as possible, and in order to do so it must lose (a) its ionic atmosphere and (b) its water envelope. It is conceivable that a metal ion may actually arrive on the lattice whilst still retaining part of its atmosphere or of its water sheath. The more rapidly a layer is built up, and deposition continued over the ion in question, the less chance will these other bodies possess of escaping back into the solution. The precise manner of cohesion of these particles to the lattice cannot be postulated at present, and no good purpose would be served by attempting to label the process "adsorption" or "van der Waals' cohesion" in the present state of our knowledge. There is, however, ample evidence that such forms of cohesion may occur, and in this way the inclusion in the deposit of water dipoles, complex cations, or undissociated molecules may take place. The colloidal bodies frequently added to depositing solutions will behave in an exactly similar manner. Further,

colloidal hydroxides which have been formed by precipitation, have been found by O'Sullivan[49] to enter the deposit and influence its structure, and it is also known that hydrogen can be codeposited with several metals, including iron, nickel, cobalt and chromium, and so disturb the regular arrangement.

Facts explained by the Hypothesis

The manner in which this hypothesis fits the facts of the case and enables us to predict a variation in structure will now be considered. Variations in structure may be due to any of the following causes:

1. The properties of the metal.
2. The properties of the anion.
3. The external conditions of deposition.

(1) *The Properties of the Metal.*

In discussing the variations in structure from metal to metal it would perhaps be more accurate to refer to the properties of the metal in its relation to the solvent. It is found in general that the metals silver, thallium, cadmium, lead and tin are prone to yield coarsely crystalline deposits from aqueous solutions. The reasons for this behaviour may be inferred from an examination of the properties of these metals. In the first place they are all metals of high atomic number. Two of them, silver and thallium, are normally univalent, and the remainder are bivalent. Silver nitrate is known to be highly dissociated, but the salts of the other metals are generally quite weak (cf. Davies[45]) and complex ion formation occurs to a considerable extent in solutions of their salts. They are all, however, believed to be hydrated to a very limited extent. Hydration is found to diminish with increasing atomic number, and to be particularly weak with univalent metals. Thus thallium should possess the smallest water sheath of the common metals, with silver lying second in ascending order of hydration. (The production of single crystals of thallium by Asahara and Sasahara[28] has already been referred to). Cadmium, lead and tin, although bivalent, will possess small water envelopes on account of their high atomic number.

Now the behaviour of these metals in solvents other than water is quite different. Kahlenberg[50] has pointed out, for instance, that silver deposited from a solution of $AgNO_3$ in pyridine yields a very finely crystalline deposit. Röhler[51] has obtained compact adherent deposits of lead, tin and zinc from solutions of their chlorides and nitrates in formamide, and Patten and Mott[52] record the preparation of smooth deposits of cadmium and tin, at low current densities, from their chloride solutions in acetone. Taft and Barham[53] carried out extensive experiments with liquid ammonia solutions, and obtained fine grained adherent deposits of lead and cadmium. Audrieth and Yntema[54] employing the same solvent, prepared smooth deposits of silver and lead from their nitrate solutions. The last-named workers recorded ammonation "in several cases," but did not indicate the particular solutions in which it occurred.

The property possessed by these metals whereby coarsely crystalline deposits are obtained from aqueous solutions, cannot therefore be a specific property of the metal, such as surface tension, or the effect would persist from solvent to solvent. The explanation should rather be sought in the specific attractive forces between the metal ion and the solvent molecules. Koch[55] has shown that molecules containing groups of an ammoniacal or nitrile character, such as pyridine, aniline, acetonitrile, have in general a greater affinity for the silver ion, than those containing hydroxylic or ketonic groups. Thus solvation may be expected to occur to a considerable degree in these solvents, and deposits obtained from them will be of a finely crystalline structure on account of the interference with the development of the lattice caused by the presence of these solvent dipoles. Thus, with the heavy metals in aqueous solution, the influence of low hydration outweighs that of feeble dissociation and consequent low metal ion concentration. With metals of lower atomic number such as copper and zinc larger water envelopes are to be expected, and although dissociation is rather more complete in their simple salts, compact deposits of a fairly fine structure are obtained.

(2) *The Properties of the Anion.*

The properties of an anion which must be considered from a deposition point of view are its charge, size, and co-ordinating tendency. The higher the valency of an anion and the greater its size, the less in general will be the degree of dissociation of its salts. The most important property from our point of view, however, is the tendency to form complex ions. This tendency is very pronounced with such ion groups as the cyanide, and leads to an exceedingly low concentration of free metal ions. Glasstone[56] has suggested that in solutions of copper and silver cyanides complex cations of the type $Cu_2CN\cdot$, $Cu_3CN\cdot\cdot$, $Ag_2CN\cdot$, $Ag_3CN\cdot\cdot$ are formed in addition to the complex anions. From the theoretical analysis of the problem of dissociation made by Koch[47] it appears to be quite probable that such cations may exist in such solutions of noble metals. Koch[57] has also shown that complex formation (ionic-molecular covalency) may be regarded as merging gradually into solvation (ionic-molecular electrovalency), and not as a distinct phenomenon. This result is of particular interest and application to the problem in hand. Fuseya and his co-workers[58] have shown by numerous experiments that complex cations may enter an electrodeposit and affect its structure to a considerable degree, and thus the conception of the inclusion of solvent dipoles introduced by the writer receives a certain amount of theoretical support.

In contradistinction to the coarse deposits of silver obtained from silver nitrate solutions and solutions of the simple salts of cadmium, those from complex cyanide solutions are very fine grained. Copper and zinc deposits from cyanide solutions are also known to be much finer grained than those from sulphate or chloride solution, and many other similar cases could be mentioned. Fuseya found that the greater the concentration of complex

ions, formed by the addition of glycocoll to solutions of copper sulphate, the finer was the structure of the deposit obtained. The size of the crystals seemed to be determined by the amount of glycocoll entering the deposits, and with increasing· current density, the amount of inclusion also decreased. Increase of temperature caused a falling off in the amount of glycocoll entering the deposit, and a slight increase in crystal size, as would be expected.

(3) *The External Conditions of Deposition.*

(a) *Current Density.*

Current density may be redefined in more fundamental terms as the number of metal ions being deposited per unit area per second. In other words, the higher the current density the less will be the time interval between the arrival of two consecutive ions at the same point on the lattice, and the greater the probability of electrolytically inert particles becoming included in the deposit. In the cases of crystallisation in general Marc[59] has shown that foreign substances adsorbed by the crystal reduce the velocity of crystallisation most markedly, and he has pointed out that this seems to suggest the existence of an adsorption layer in which the essential process of crystallisation occurs. But in the case of electrodeposition the current density will not permit of a retardation in crystallisation, and so in all probability inclusion of the foreign substance and consequent nucleus formation will result.

(b) *Temperature.*

Increase of temperature, besides causing an increase in speed of diffusion, will also produce an all-round increase in mobility. The proportion of metal ions to other bodies in the cathode film will be increased, and there will probably also be less tendency for the foreign particles to adhere to the cathode. The chances of inclusion of dipoles or molecules are thus considerably reduced by increase of temperature, and crystal growth will be favoured. Graham[29] found that the increase of grain size obtained by a small increase of temperature was greater than would be expected from the decrease in polarisation. The latter effect will be due to the increased metal ion supply, and it may therefore be concluded that the tendency of foreign particles to adhere to the cathode is also reduced to some extent. Further, the preparation of deposits which reproduce the cathode structure is favoured by increased temperature. In this case, of course, inclusions are absent from the deposits.

(c) *Agitation.*

A similar result may be obtained by assisting the process of diffusion by external mechanical means. By stirring a solution, or by moving the cathode, a fresh supply of metal ions can be brought into the diffusion layer, with the usual result of increase in grain size of the deposit. The effect of agitation is more pronounced in dilute than in concentrated solutions for a given current density. Now agitation will restore the concentration of metal ions to the cathode film, without appreciably affecting that of the other constituents. The effect will therefore be the same as if a higher concentration of metal ions was being employed, without the attendant increase in the

concentration of undissociated molecules, complex ions, etc. Thus if a dilute solution is used with agitation it would be expected from the theory that conditions would be favourable to crystal growth. Agitation thus acts in the opposite sense to increase of current density, by favouring the rapid attainment of equilibrium in the cathode film even when this is quite dilute with respect to metal ions. Hirata,[21] as previously mentioned, found that low concentration favoured regular orientation if accompanied by low current density. In this case the natural agitation was sufficient to supply the requisite concentration of metal ions, whilst the concentration of other particles was kept very low.

(d) *The Presence of Colloidal Matter.*

The effects obtained by the adsorption of colloidal matter in the deposit are too well known to need discussion. The excellent paper of Förster and Deckert[60] gives a complete survey of adsorption phenomena of this type, and Taft and Messmore[61] have also recently concluded that the effect of gelatin in copper sulphate electrolytes is due to adsorption.

Conclusion

It must be impressed again that there is nothing of finality about the hypothesis advanced above. Much more work remains to be done both in the field of electrolytic solutions and that of electrodeposition before a really complete account can be given of their interconnection in the subject under discussion. The confirmatory evidence that has been submitted does not represent the whole of that available, but has been restricted to simple considerations of one factor at a time. In actual practice all these factors act together and it is difficult to distinguish or isolate the effect of any one variable. Outstanding difficulties are inevitable in a theory embracing a subject about which little is definitely known, but the writer will be content if he has succeeded in the present paper in bringing the science of electro-deposition up to date with the modern solution theory.

References

[1] Dept. of Scientific & Ind. Research, Bull. 6 (1922).
[2] Z. Kristall., 1, 453 (1877).
[3] Rec. Trav. chim., 39, 720 (1920).
[4] Trans. Am. Electrochem. Soc., 44, 397 (1923).
[5] Z. Elektrochemie, 31, 649 (1925).
[6] Trans. Am. Electrochem. Soc., 45, 229 (1924).
[7] J. Chem. Soc., 1926, 2887.
[8] Z. physik. Chem., 139, 597 (1928).
[9] Z. physik. Chem., 142, 97 (1929).
[10] Z. physik. Chem., 102, 267 (1922).
[11] Z. Elektrochemie, 27, 45 (1921).
[12] Rec. Trav. chim., 50, 339 (1931).
[13] Trans. Faraday Soc., 1, 324 (1905).
[14] Trans. Am. Electrochem. Soc., 44, 305 (1923).
[15] J. Chem. Soc., 1927, 1077.
[16] J. Chem. Soc., 1929, 690.

[17] Z. Elektrochemie, **31**, 655 (1925).
[18] Trans. Am. Electrochem. Soc., **49**, 369 (1926).
[19] Phys. Rev., (2) **26**, 390 (1925).
[20] Mem. Coll. Sci. Kyoto, **10**, 95 (1926).
[21] Mem. Coll. Sci. Kyoto, **11**, 429 (1928).
[22] J. Inst. Metals, **7**, 123 (1912).
[23] J. Inst. Metals, **8**, 149 (1912).
[24] Trans. Faraday Soc., **24**, 147 (1928).
[25] Z. anorg. Chem., **121**, 275 (1922).
[26] Bull. Acad. Sci. U.S.S.R., **9**, 777 (1929).
[27] Nature, **128**, 912 (1931).
[28] Sci. Papers Inst. Phys. Chem. Res. Tokyo, **5**, 79 (1926).
[29] Trans. Am. Electrochem. Soc., **52**, 157 (1927).
[30] Trans. Faraday Soc., **24**, 387 (1928).
[31] Trans. Faraday Soc., **25**, 590 (1929).
[32] Trans. Faraday Soc., **27**, 309 (1931).
[33] Phil. Mag., **11**, 1009 (1931).
[34] J. Am. Chem. Soc., **35**, 804 (1914).
[35] J. Am. Chem. Soc., **39**, 1906 (1917).
[36] Am. Chem. J., **41**, 208 (1909).
[37] Z. physik. Chem., **58**, 301 (1907).
[38] Z. Elektrochemie, **15**, 602 (1909).
[39] Z. Elektrochemie, **16**, 967 (1910).
[40] J. Am. Chem. Soc., **52**, 1000 (1930).
[41] Z. physik. Chem., **47**, 161 (1930).
[42] Physik. Z., **24**, 185 (1923).
[43] Trans. Faraday Soc., **23**, 357 (1927).
[44] Trans. Faraday Soc., **23**, 354 (1927); **26**, 592 (1930).
[45] Trans. Faraday Soc., **27**, 621 (1931).
[46] J. Chem. Soc., **1931**, 1998.
[47] Phil. Mag., **11**, 1122 (1931).
[48] Trans. Electrochem. Soc., **59**, 105 (1931).
[49] Trans. Faraday Soc., **26**, 89 (1930).
[50] Trans. Am. Electrochem. Soc., **44**, 423 (1923).
[51] Z. Elektrochemie, **16**, 419 (1910).
[52] Trans. Am. Electrochem. Soc., **15**, 529 (1909).
[53] J. Phys. Chem., **34**, 929 (1930).
[54] J. Phys. Chem., **34**, 1903 (1930).
[55] J. Chem. Soc., **1928**, 269.
[56] J. Chem. Soc., **1929**, 690.
[57] Phil. Mag., **10**, 559 (1930).
[58] Trans. Am. Electrochem. Soc., **50**, 235 (1926); **52**, 249 (1927).
[59] Z. physik. Chem., **66**, 385 (1908); **67**, 470 (1909).
[60] Z. Elektrochemie, **36**, 901 (1930).
[61] J. Phys. Chem., **35**, 2585 (1931).

The Laboratory,
Vauxhall Motors, Ltd.
Luton.
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THE APPARENT VOLUMES OF SALTS IN SOLUTION

III. Saturated Solutions of Mixed Electrolytes

BY ARTHUR F. SCOTT

Although there is a very extensive literature dealing with the effect of an added electrolyte on the properties of a saturated solution of a second electrolyte, very little attention has been paid to the apparent molal volumes of the salts in such solutions. Nicol,[1] in one of his pioneer studies of solubility relationships examined this property of the solutes for a few salt pairs. His conclusions, expressed in our present terminology, were that in a majority of cases the apparent volumes of salts in a solution saturated with both of them, are the same as in saturated solutions of the individual salts. Very similar conclusions were reached by Masson[2] from an investigation of the volume changes which occur on the addition of acid to saturated salt solutions. From his expression for the variation of the density of these solutions as functions of both acid and salt concentrations Masson found, assuming the density of water in solution to be that of the pure solvent, that over a wide range of concentration "the molecular volumes of the solutes are independent of their concentration" and "that in this respect mixed electrolytes differ from single electrolytes, the molecular volumes of which vary considerably with concentration." To extend the applicability of his density formula to high concentrations Masson was forced to assume that the molecular volume of water in solution was different from that of the pure liquid and, by taking a special value of the density of water for each solution, he was able to show that the calculated densities of the acid-salt solutions were in good agreement with the experimental data. Recently, in a series of papers Ingham[3] has employed this expression of Masson to study the apparent hydration of ions. That the apparent molal volumes of solutes in saturated solutions of mixed electrolytes are in some instances independent of each other and of concentration was also pointed out in a previous article[4] and was offered as evidence in support of a tentative hypothesis of the significance of the apparent molal volumes of salts in solution.

The object of the present study is to investigate this question of the apparent volumes of salts in solutions saturated with respect to one of them. While the scope of the study is somewhat restricted by the lack of sufficiently precise measurements, adequate data are available for a number of mixtures

[1] Nicol: Phil. Mag. 17, 547 (1884). A more complete paper on the subject, which Nicol refers to later [Phil. Mag. 31, 369 (1891)] as forthcoming, cannot be found by the writer.

[2] J. I. O. Masson: J. Chem. Soc., 99. 1132 (1911).

[3] Ingham: J. Chem. Soc., 131, 1917, 2381 (1928); 132, 2059 (1929); 133, 542 (1930).

[4] Scott: J. Phys. Chem., 35, 3379 (1931). At that time the writer did not know of the paper by Nicol and was not acquainted with the general conclusions of Masson. In fact the validity of the rule for two cases to be discussed subsequently was noted about two years ago in connection with a study of the apparent molal volumes of salts in saturated solutions. [Scott and Durham: J. Phys. Chem., 34, 2035 (1930).]

of uni-univalent salts, which are pretty much varied with regard to the type of ion involved. From the examination of these data it appears that the following conclusions are permissible: First, the apparent molal volumes of the electrolytes are not dependent directly on the amount of water present in the solution. And second, the results can be interpreted to mean that in every case the apparent molal volume of the saturating salt has the value which is characteristic of the saturated solution of the single salt; and that the apparent volume of the added electrolyte either (1) is the same as when it is the saturating salt (rule of Nicol) or (2) has some different but definite value.

Before undertaking to discuss the data from which the above conclusions are drawn it is desirable to review briefly the salient features of the aforementioned hypothesis because, in spite of its provisional nature, it not only affords a plausible basis for the understanding of the conclusions in question but also suggests other incidental lines of analysis for consideration. This hypothesis, it may be recalled, follows the customary procedure of other discussions of this subject in assuming that the apparent molal volume ϕ of a solute in very dilute solutions is equal to the domains of the solute ions less the contraction in volume suffered by the solvent water molecules. It differs, however, from other hypotheses in the fundamental assumption that only the solvent molecules directly adjacent to the ions undergo contraction. According to this viewpoint the increase in ϕ with increasing concentration is to be attributed to the disturbance of the water molecules in contact with the ions. A possible cause[1] of this disturbance may be realized in the association of the solute ions to form pairs or clusters with the consequent displacement of the solvent molecules. The importance of our basic assumption lies in the fact that the amount of contraction of the solvent (and thus the magnitude of ϕ) is made dependent not on the total quantity of solvent present in the solution but on the state or what, in accord with the mechanism suggested above, may be termed the "degree of association" of the solute ions.

We may now consider the bearing of this hypothesis on those properties of the ϕ values in saturated solutions which we have already summarized. In the first place we may note that the absence of a direct relationship between the ϕ values and the amount of solvent present is in harmony with our fundamental postulate. In the second place the fact that the ϕ value of the saturating salt is constant may be taken to mean that when, at a given temperature, a solid salt is in equilibrium with a solution, its state or degree of association in the solution is definitely fixed and is not affected by the addition of a second electrolyte. Finally, since the ϕ value of the added electrolyte in a given solution is constant, we must suppose that its state is the same, regardless of concentration. However, since the ϕ value of the added electro-

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[1] A similar suggestion has been put forward recently by Butler and Lees. [Proc. Roy. Soc., **131 A**, 389 (1931).] Commenting on the fact that the molecular refractivity of lithium chloride is constant whereas its apparent volume increases with concentration, they write: "It may be suggested that a possible cause of the effect might be found in collisions between two ions, which become more frequent as the concentration is increased, and cause a certain amount of disorientation of the sheaths of solvent molecules carried by them, and thus give rise to an increase of volume."

lyte is found to be different in different solutions, we must conclude that its state is determined to some extent by the nature of the saturating salt.

Having outlined briefly the viewpoint which we shall adopt we may now take up the detailed examination of the experimental data upon which our conclusions are based. The apparent molal volume ϕ of a salt is defined by the expression:

$$\phi = V - nv_1 \tag{1}$$
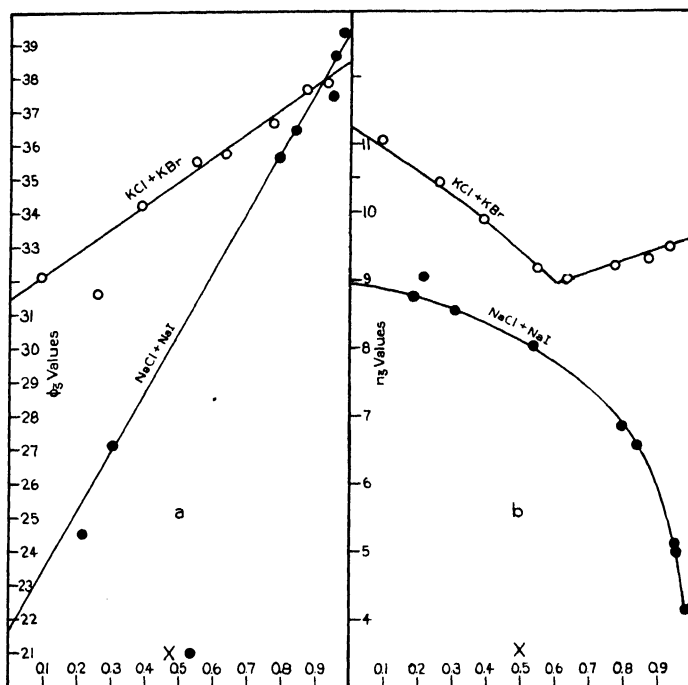
FIG. 1

Plot showing the Variation with molecular composition of the solute in a saturated solution of (a) the Apparent Molal Volume and (b) the number of mols of solvent per mol of total solute.

where V is the volume of a solution containing one gram-mol of the salt; n is the number of mols of water present in the solution; and v_1 is the volume of one mol of the pure solvent at the temperature of the solution. In dealing with saturated solutions containing two electrolytes we shall find it convenient to employ the apparent molal volume of the mixed salts, which we shall designate as ϕ_s. This quantity is calculated on the condition that the total number of mols of the two solutes in the saturated solution equals unity. The fraction of a mol of one solute in such a solution will be indicated by x. Thus, if there are x_1 mols of the X_1 solute and x_2 mols of the X_2 solute in the given solution, ϕ_s corresponds to a solution in which $x_1 + x_2 = 1$. The quantities V_s and n_s will refer, of course, to saturated solutions which satisfy the same condition.

The first type of mixtures which we shall consider will be that which appears to be the simplest. The necessary data for the two available examples are given in Table I. In Fig. 1b the n_s values of the two salt pairs are plotted against the corresponding x values. This convenient method of portraying the isothermal relationships in a ternary system is essentially that proposed by Jänecke.[1] The minima of the drawn curves represent, of course, the eutectic points of the saturated solutions where both salts as solids are in equilibrium with the solution phase. Analogous to the above graph is Fig. 1a in which the ϕ_s values of the salt mixtures are plotted against the corresponding x quantities. In this case the plotted points appear to fall on a straight

<div align="center">

TABLE I

Values of x, ϕ_s and n_s for two Salt Mixtures

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KCl–KBr at 25°[1]			NaCl–NaI at 35°[2]		
x_{KBr}	ϕ_s	n_s	x_{NaI}	ϕ_s	n_s
0.000	36.6	11.23	0.000	21.7	8.97
0.093	32.1	11.05	0.187	—	8.74
0.260	31.6	10.43	0.216	24.5	9.04
0.390	34.2	9.89	0.303	27.1	8.54
0.549	35.5	9.17	0.535	21.0	8.02
0.635	35.7	9.02	0.797	35.6	6.84
0.775	36.6	9.21	0.840	36.4	6.56
0.871	37.6	9.31	0.950	37.4	5.11
0.934	37.8	9.49	0.956	38.6	4.99
1.000	38.4	9.68	0.981	39.3	4.14
			1.000	39.3	4.22

[1] Fock: Taken from Comey's "Dictionary of Chemical Solubilities," page 745. The calculated value of ϕ_s for the saturated solution of KCl is obviously in error. See Table II.
[2] From unpublished measurements made in this laboratory with Dr. E. J. Durham.

line passing between the ϕ_s values of saturated solutions containing only a single salt. Since the deviations which do occur are in most instances toward the extremes where the amount of one component solute relative to the other is small, they are most likely the consequence of errors in the basic solubility measurements. For such errors would be greatly magnified in calculating the plotted quantities.

From the linear relationships depicted in Fig. 1b it follows that for the two cases under consideration the apparent molal volume of each salt is independent of the other salt present regardless of which one is the saturating salt. Furthermore, a comparison of the two plots (Figs. 1a and 1b) shows quite clearly that there is no close connection between the apparent molal volumes of the salts and the number of mols of water present in the solution. In short, these two examples conform to the rule which was derived from the conclusions of Nicol. We have already interpreted the above results to mean (1) that the state or degree of association of the saturating solute is unaffected

[1] Jänecke: Z. physik. Chem., **51**, 132 (1906).

by the presence of the added electrolyte and (2) that the added electrolyte is in the same state as when it is the saturating salt. Regarding the condition of the electrolyte in the assumed state we cannot, however, draw any definite conclusions.

Only the above two examples will be presented to show that the apparent molal volumes of solutes in saturated solutions are independent of each other and also of the number of mols of water in the solution. While the data of other salt pairs, which might be expected to belong to the same type of those

<div align="center">TABLE II</div>

Values of x, ϕ_s, n_s for Three Chloride-Hydrochloric Acid Mixtures at 25°

HCl–KCl			HCl–NaCl			HCl–NH₄Cl		
x_{HCl}	ϕ_s	n_s	x_{HCl}	ϕ_s	n_s	x_{HCl}	ϕ_s	n_s
0.000	31.7	11.43	0.000	21.6	8.99	0.000	39.6	7.50
0.110	30.1	11.47	0.093	21.2	9.11	0.076	38.0	7.51
0.231	28.7	11.35	0.165	21.2	9.14	0.179	36.0	7.61
0.341	27.6	11.12	0.418	20.8	9.07	0.293	33.7	7.60
0.413	26.2	11.02	0.580	20.6	8.93	0.317	33.1	7.61
0.584	24.7	10.42	0.627	21.1	8.80	0.352	32.6	7.60
0.711	23.2	9.74	0.681	20.2	8.72	0.507	29.6	7.40
0.766	22.5	9.32	0.771	20.5	8.35	0.568	28.6	7.25
0.832	22.0	8.65	0.853	20.5	7.86	0.608	27.8	7.14
0.903	21.1	7.65	0.918	20.4	7.20	0.686	26.3	6.85
0.959	22.0	6.21	0.960	20.6	6.38	0.784	24.4	6.28
0.969	21.0	5.20	0.981	20.7	5.67	0.826	23.7	5.91
0.981	21.2	3.90	0.990	20.8	4.78	0.874	22.9	5.38
0.983	21.4	3.45	0.999	21.7	2.92	0.918	22.4	4.34
0.982	21.5	3.33				0.936	22.4	3.46
0.983	21.7	2.99				0.937	22.7	2.75

we have just considered, are to be found in solubility tables, they are for the most part so obviously irregular as to be worthless for our present purpose.

We shall now turn to a different class of salt mixtures which are characterized by the fact that the linear relationship analogous to that of Fig. 1a shows one or more definite discontinuities. To introduce this type of mixtures we may consider first the changes which take place on adding an acid to a saturated salt solution, a phenomenon which has received a great deal of attention. In Table II are given the values of x, ϕ_s, and n_s for three different chloride-hydrochloric acid mixtures calculated from the measurements of Ingham. A plot of these quantities is shown in Figs. 2a and 2b. These graphs reveal that in these cases also the value of ϕ_s is not related in any obvious way to n_s, the amount of water present in the saturated solution. Furthermore, within the limits of experimental error[1] the plotted points fall on a straight

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[1] Although the magnitude of the experimental error is not known exactly, its effect on the derived ϕ_s quantity must amount to approximately 0.2 cc. Values of ϕ_s for saturated solutions of KCl and NaCl at 25° have been found from careful measurements in this laboratory to be 31.3 cc. and 21.4 cc., respectively. The lines as drawn in Fig. 2b pass through these values.

line up to an acid concentration which is rather high relative to the salt concentration and also in terms of molarity. In the case of HCl–KCl solution the $x = 0.903$ point, which falls on the line, corresponds to an acid concentration of 5.67 mols per liter. With the HCl–NH$_4$Cl solutions the $x = 0.874$ point represents a solution in which there are 7.35 mols HCl per liter. The data for the HCl–NaCl solutions appear to be most irregular but the $x = 0.771$ point is for a solution which is 4.50 molar with respect to the acid. Unfortunately the data are not sufficiently precise to permit the determination of the exact point at which the ϕ_s values deviate from the linear relationship.

To interpret this linear relationship we can assume what was concluded from the previous examples, that the apparent molal volume of the saturating salt is unaffected by the presence of the acid and that the acid in the salt solution has a constant value of ϕ. To determine the ϕ value of the added acid we can extrapolate the drawn lines to the limiting $x = 1.00$ value. The fact that the three drawn lines have a common intercept ($\phi = 20.0$) can be taken to indicate that the added acid is in the same state or degree of association in the three saturated salt solutions.

A step toward the determination of the properties of the hydrochloric acid solution, characterized by the condition that $\phi = 20.0$, would be to calculate the composition of such a solution. This can be accomplished by means of the following empirical equation of Masson:[1]

$$\phi = k \, m^{1/2} \times \phi_0 \qquad (2)$$

In this equation m is the molarity in mols per liter, and k and ϕ_0 are constants. These two constants for hydrochloric acid solutions at $25°$ have been found by Geffcken[2] to be 0.83 and 18.20, respectively. Introducing the above values of ϕ, k, and ϕ_0 into equation 2 the molarity m of the solution is calculated to be 4.71. Hence the volume of the solution which contains one mol of HCl is 213 cc. Now from equation 1, taking the volume of one mol of water to be 18.1, we find n, the number of mols of water present in the solution, to be 10.7. This figure, however, can be only an approximate estimate because a very slight change in the value of ϕ produces a large variation in the calculated value of n. Thus, following the above procedure the following values of n have been calculated for different values of ϕ: $\phi = 19.9$, $n = 12.1$; $\phi = 20.0$, $n = 10.7$; $\phi = 20.1$, $n = 9.5$. In view of this uncertainty we can only take 11 as the approximate number of mols of water present in the limiting acid solution.

While it is true that the foregoing calculations do not give any information regarding the state of the acid electrolyte when its apparent molal volume is 20.0, we may reasonably suppose that this state is identified with a solution which contains 11 mols of water for one mol of HCl. This supposition would lead to the conclusion that, so long as the ϕ value of the acid is 20.0, each mol of the added acid will have associated with it 11 mols of water. In other words

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[1] Masson: Phil. Mag., (7) **8**, 218 (1929). The writer has discussed this equation in two previous papers of this series: J. Phys. Chem., **35**, 2315, 3379 (1931).

[2] Geffcken: Z. physik. Chem., **155**, 1 (1931).

we may look upon this figure 11 as the number of mols of "fixed" water associated with or appropriated by each mol of acid when added to the saturated salt solutions. This interpretation of the calculated value of n makes it practically equivalent to what is generally termed the "hydration number" of the solute, and accordingly it may be designated as n_h.
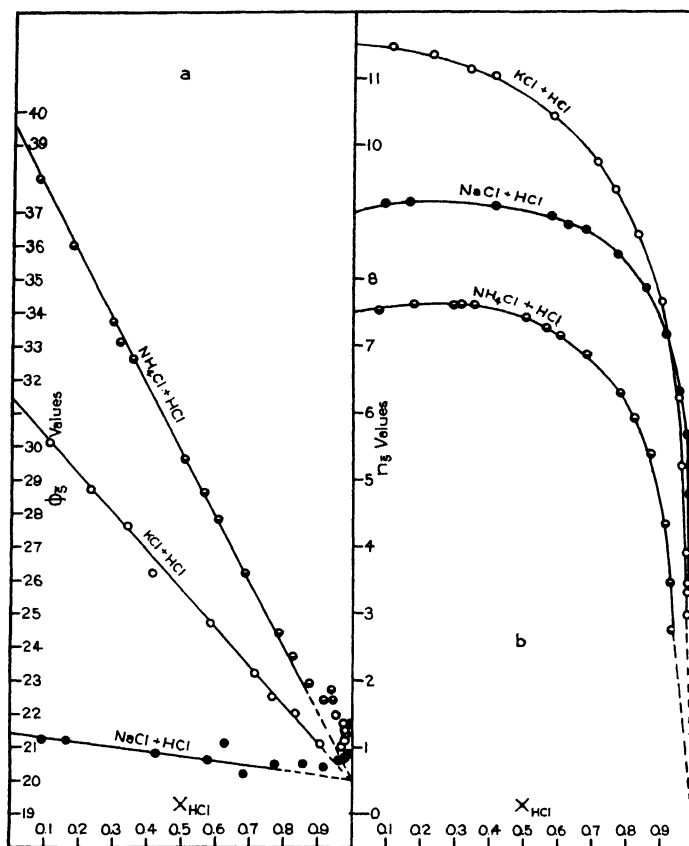
FIG. 2

Graphic representation of the Effect of HCl on (a) the ϕ_s and (b) the n_s quantities of three Saturated Solutions.

The salting-out effect[1] has frequently been investigated as a means of determining the hydration of the added electrolyte. The present value (11) for hydrochloric acid is, with one exception, much higher[2] than the values obtained from the effect of the acid on the solubility of a given substance and is also higher than the values estimated from the results of the other methods which have been studied for this purpose. The exception noted above is,

[1] For a summary and criticism of this method see Washburn: Jahrbuch der Radioaktivität und Elektrotechnik: **5**, 516 (1908).

[2] For instance, Washburn cites 2.7 as the maximum number of mols of water appropriated by HCl, as determined from its effect on the solubility of gases.

however, of considerable interest. Bjerrum,[1] in order to account for the variation in the activity coefficients of strong electrolytes with concentration, assumed that the ions of the completely dissociated electrolyte are hydrated and from the equation established on the basis of this assumption he estimated the hydration numbers of a number of electrolytes. Using the activity of HCl as determined from freezing point measurements he estimated the hydration number of the acid to be 9, the figure also obtained from the electromotive force data of dilute acid solutions. On the other hand, employing activity values obtained from other electromotive force measurements n_h for H^+ was calculated to be 9 and n_h for Cl^-, 2, a total of 11. Because of the approximations involved in his calculations Bjerrum accepted 10 as the approximate value of the hydration number of HCl but observed that if association of water were to be taken into account, slightly larger values would be obtained. Calculations of the n_h values of HCl by Schreiner,[2] which were likewise based on Bjerrum's equation, yielded essentially the same results as those we have already noted.

The actual volume (ϕ_s) of HCl when x = 1.00 cannot be determined from Fig. 2b because of the fluctuations exhibited by the plotted points. However, when the ϕ_s values of a given solution are plotted against the corresponding n_s values, it is possible, by extrapolating over a very short range, to get the value of ϕ_s for the case where n_s equals zero. This limiting quantity for the three solutions under consideration is approximately 23.5 cc., a minimum figure. Since n_s, when x = 1.00, appears to be zero, the estimated value of ϕ_s may be the desired limiting value. In any case, because the quantity in question represents the volume of HCl when it is in the solution state but with no water present, it may be compared with the volume of pure HCl under various conditions. Some data of interest in this connection, which are based on measurements made or cited by Simon and Simson,[3] are given below:

Temp.	State	Volume	Structure
80° Abs.	solid	< 24.2 cc.	molecular lattice
98° Abs.	solid	— —	transition point
07° Abs.	solid	24.8 cc.	face-centered cubic
62° Abs.	liquid	28.5	melting-point

It is evident that the value 23.5 cc. approximates that of the solid rather than the liquid state. Some evidence that the limiting volume does not correspond to that of the polar lattice structure might be derived from the following considerations. A limiting value ϕ_m can be calculated from equation 2 by imposing the condition that $m_m = 1000/\phi_m$ and represents the solution state at which the apparent volume of the solute is identical to the volume in which it is contained (n = 0 in equation 1). For solutions of HCl this quantity is

[1] Bjerrum: Z. anorg. Chem., 109, 275 (1920). A more general derivation of Bjerrum's equation and a discussion of it is to be found in Taylor's "Treatise of Physical Chemistry," Vol. II (first edition), page 775.

[2] Schreiner: Z. anorg. Chem., 135, 333 (1924); 166, 219 (1927).

[3] Simon and Simson: Z. Physik, 21, 168 (1924).

23.6 cc. and is practically the same as that found from the ϕ_s-n_s graph. However, in the second paper of this series reasons were advanced to show that for solutions of the polar alkali halide salts the ϕ_m state was not the state at which n equals zero. If HCl solutions were assumed to conform to the same rule as that found to hold for the salt solutions, the limiting value of ϕ can be calculated and the figure obtained is 22.4 cc. Since this figure is so much lower than the minimum 23.5 cc., it may be taken to indicate that solutions of HCl are not analogous to those of the alkali halide salts.
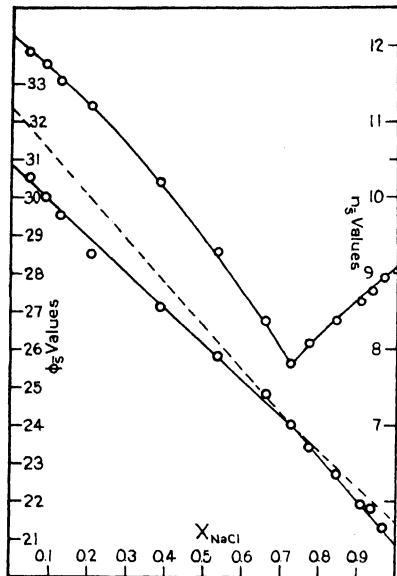
FIG. 3

Plot showing the Variation of ϕ_s and n_s quantities with the mol fraction of NaCl in the Solute, KCl + NaCl.

The general conclusions which the foregoing discussion suggests may be summarized briefly at this point. First, when hydrochloric acid is added to a saturated solution of the chloride salt, the acid appears to appropriate or require 11 mols of water. Second, the pure acid when in the solution state but not associated with water appears to have properties resembling those of the solid, possibly the modification with a molecular lattice structure. The nature of the change which takes place when the acid goes from one of the above states to the other is, of course, unknown. However, it may be observed that the ϕ_s-n_s plot reveals two discontinuities the study of which with more precise data might throw some light on this question.

We may next consider the salt pair KCl–NaCl. In Table III are the necessary values of x, ϕ_s, and n_s calculated from the published measurements of Holluta and Mautner.[1] The plots showing the relationships of these quantities are given in Fig. 3. Here again, despite the break in the ϕ_s-x line at the eutectic point, it is obvious that the variation in the apparent volumes of the solutes is not directly related to the amount of water present in the saturated solution.

An analysis of the ϕ_s-x plot may be carried out in the manner described in the discussion of the preceding example. When NaCl is added to a saturated solution of KCl, it has, according to our argument, the properties of a solution whose ϕ value is 21.5 (x = 1.00). Using equations 1 and 2 the value of n_h is computed to be 7.7 or 8. For the purpose of these calculations the constants k and ϕ_0 of equation 2 at 18.5° were determined from the measurements of Kohlrausch and Hallwachs[2] to be 2.24 and 15.9, respectively.

The value of ϕ which characterizes KCl as the added electrolyte is 32.3 cc. and, as in the case of NaCl, represents a concentration greater than that of

[1] Holluta and Mautner: Z. physik. Chem., **127**, 464 (1927).

[2] Kohlrausch and Hallwachs: Z. physik. Chem., **12**, 538 (1893).

the saturated solution. No data have been found by which to determine the constants k and ϕ_0 which are necessary for the calculation of n_h. The following method, however, appears practicable as a means of estimating the values of these constants. In the first paper of this series values of k and ϕ_0 are given for both NaCl and KCl solutions at $0°$, $25°$, and $50°$. Geffcken in his article gives in addition to these values, values of the same constants at $35°$ and $45°$. Now, when the k values of the KCl solutions are plotted against those of the NaCl solutions at the same temperatures, the

TABLE III

Values of x, ϕ_s and n_s for Two Mixtures at $18.5°C$

KCl–NaCl			KCl–KNO₃		
x_{NaCl}	ϕ_s	n_s	x_{KNO_3}	ϕ_s	n_s
0.000	30.8	12.13	0.000	30.8	12.13
0.043	30.5	11.91	0.043	31.4	11.68
0.086	30.0	11.75	0.082	32.1	11.18
0.127	29.5	11.58	0.119	32.5	10.79
0.206	28.5	11.20	0.188	33.5	9.99
0.388	27.1	10.20	0.265	34.4	9.16
0.536	25.8	9.28	0.288	34.8	9.82
0.660	24.8	8.36	0.368	35.4	10.60
0.727	24.0	7.80	0.497	36.3	12.99
0.772	23.4	8.07	0.708	38.1	15.91
0.845	22.7	8.36	0.814	39.3	17.11
0.908	21.9	8.62	0.874	40.0	17.64
0.936	21.8	8.75	0.934	40.5	18.29
0.969	21.3	8.93	1.000	41.3	18.78
1.000	20.9	9.08			

plotted points fall closely on a straight line, a fact which means that the ratio of the temperature coefficients of these constants is independent of temperature.[1] The point on this line corresponding to an abscissa value of 2.24 is 2.42 and may be accepted as the k value of KCl solutions at $18.5°$. A similar relationship appears to hold also for the ϕ_0 constants, and the value of ϕ_0 for KCl solutions at $18.5°$ estimated in this way is 26.0 cc. The above relationships cannot be established as a general rule without a more extensive test. In the present case, however, the estimated values of the constants can be checked indirectly. Thus, if for the saturated solution of KCl ϕ_s is taken to be 30.8 (Table III), n_s is calculated to be 12.3, a figure which agrees reasonably well with 12.1, the value given in the table. Employing these same constants and taking ϕ_s to be 32.3, n_h for the added KCl is computed to be 6.4, or 6.

These approximate n_h values, 8 for NaCl and 6 for KCl, may be compared with other estimates. The corresponding values given by Washburn are

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[1] For a discussion of a relationship of this character for the temperature coefficients of solubility see Scott: J. Phys. Chem., **33**, 1000 (1929).

10.5–9.5 and 9.0–8, as determined from the salting-out effect of these salts on the solubility of hydrogen, and in both cases they tend to decrease with increasing concentration of the added salt. Sugden[1] on the basis of distribution measurements estimated n_h for NaCl to be 8 and that for KCl to be 3.4.
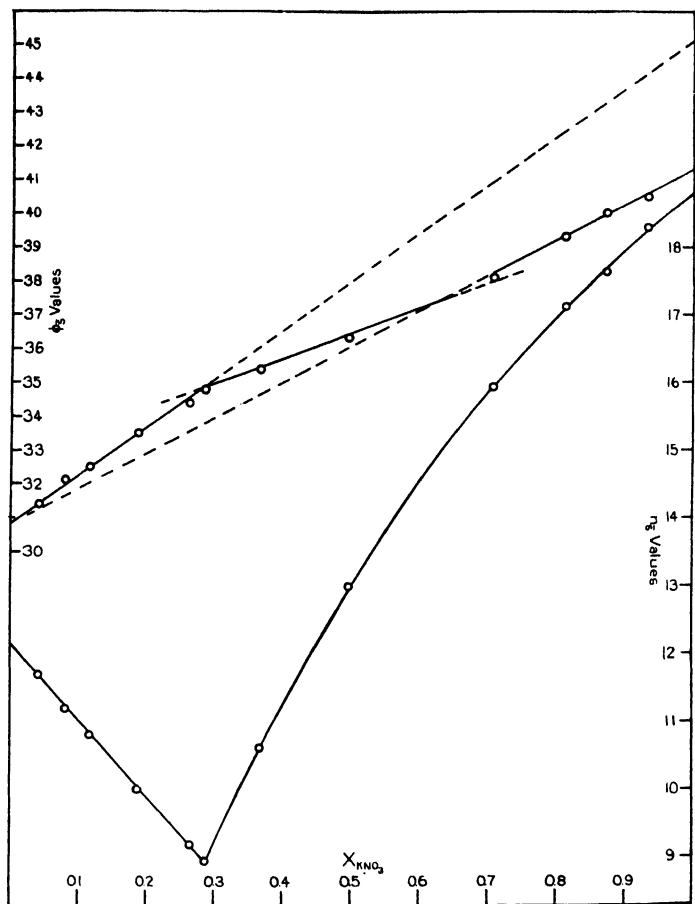
FIG. 4
Plot showing the Variation of ϕ_s and n_s with the mol fraction of
KNO$_3$ in the solute KCl + KNO$_3$

Bjerrum from his theory calculated the hydration number for KCl to be 2. The order of magnitude of these comparison values is seen to be the same as the n_h values calculated by our present method, a fact which strengthens the interpretation we have placed on the latter quantities.

In concluding this discussion of the KCl–NaCl mixture it should be pointed out that these salts as added electrolytes have different properties from what was found to be the case with the KCl–KBr and NaCl–NaI mix-

[1] Sugden: J. Chem. Soc., **129**, 178 (1926).

tures. In the latter cases both KCl and NaCl on addition to saturated solutions were shown to be in the same state as in their own saturated solutions while in the present example both salts apparently are in a state which corresponds to a solution more concentrated than the saturated state. This difference in properties would seem, on the basis of the limited evidence at hand, to depend on whether the cation or anion of the added electrolyte is the same as that of the saturating salt. That no general rule regarding this condition can be formulated at this time will be evident from the results obtained with the following example.

The last case of mixed electrolytes we shall consider is the combination KCl–KNO$_3$. The necessary data are included in Table III and are taken from the same source as the KCl–NaCl data. The usual plot of the x, ϕ_s, and n$_s$ values is shown in Fig. 4. Again it is evident that the values of ϕ_s bear no direct relationship to the number of mols of water present in the saturated solution.

Although the salts of the present mixture have a common cation and therefore might be expected to resemble a mixture such as KCl–KBr, a comparison of the two ϕ_s-x graphs shows that they are by no means similar. We may consider first KNO$_3$ as the added electrolyte. Its limiting value is found to be 45.2 cc. Unfortunately, the constants of equation 2 for 18.5° are not known and consequently it is impossible to compute the composition of the solution corresponding to this value of ϕ. However, as an estimate based on the constants given by Masson for solutions of KNO$_3$ at 15° n$_h$ is calculated to be 4. Because of the small amount of water present in this hypothetical solution the calculated value of n$_h$ would not be greatly affected by small changes in temperature and is therefore approximately correct for 18.5°. A comparison of the present result with other estimates is only partially satisfactory. From the effect of KNO$_3$ on the solubility of gases the hydration number of this salt, as given by Washburn, is found to vary from 3 to 9. On the other hand Sugden on the basis of his measurements was forced to ascribe a negative value -2.7 to n$_h$. In his article Sugden lists several examples where KNO$_3$ as an added electrolyte exerts an abnormal effect in that it tends to increase the solubility of the saturating salt. From our present standpoint, however, this salt appears abnormal only in its divergence from the general rule, which was noted with the first type of salt mixtures, that when the added electrolyte has a cation in common with the saturating salt its ϕ value is the same as in its saturated solution.

On the other hand when KNO$_3$ is the saturating salt there is fairly definite evidence that the electrolyte has abnormal properties. In Fig. 4 it can be seen that on the first addition of KCl the relationship between the two solutes is the same as what was found for the case where KCl is added to a saturated solution of KBr. In short, over this range both solutes have properties in accord with the general rule. However, after the amount of KCl relative to that of the saturating salt passes a certain value there appears to be a decided change in the properties of both solutes. Although the applicability of our present method of analysis to this range of the ϕ_s-x plot is uncertain, the con-

clusions to be derived from it may be pointed out. The n_h value of the added electrolyte KCl is found to be 5–6 and is therefore similar to the value found from the KCl–NaCl data. But the amount of water estimated to be required by the saturated solution of KNO_3 is roughly 32 mols, a value which is almost twice the actual value. Hence, it would appear that the irregular variation of ϕ_s on the addition of KCl to the saturated solution of KNO_3 is due primarily to some abnormal condition of the latter electrolyte.

No conclusion can be drawn regarding the nature of the change which it is assumed KNO_3 undergoes when sufficient KCl is added to its saturated solution. It may be observed, however, that with respect to many of its properties in solution KNO_3 is regarded as an abnormal electrolyte. As an illustration of this fact Sugden, in the paper already quoted, cites the fact that solutions of this salt have "negative" viscosities. That the condition of this solute in the saturated state differs in some way from the conditions of the simpler alkali halides in the saturated state is indicated also by the following. It has been shown[1] for saturated solutions of a number of alkali halide salts that the apparent molal volume ϕ_s is linearly related to the square of the number of mols of water present in the solution at the same temperature. It was found that saturated solutions of $NaNO_3$ also conform to this rule. However, saturated solutions of KNO_3 and the heavier alkali nitrates are irregular in that the apparent molal volume varies not with the square of but directly with the number of mols of water. This exceptional property of the nitrates will be discussed in more detail in a subsequent article.

Summary

The present paper is a preliminary study of the apparent molal volumes of salts in saturated solutions of mixed electrolytes. A simple method is described for the analysis of the experimental data and is applied to some typical mixtures. Because of the limited number of cases considered no definite generalization can be established. It appears, however, that the two following classes of added electrolytes can be distinguished, assuming that the apparent molal volume ϕ of the saturating salt remains unchanged on the addition of the second electrolyte: (1) when the added electrolyte has a cation in common with the saturating salt, its apparent volume is the same as when it is the saturating salt; and (2), when the added electrolyte has an anion in common with the saturating salt, its apparent volume has a unique but constant value. Potassium nitrate was found to be an exception to these rules. The possibility of calculating the hydration number of the added electrolyte is discussed.

The Rice Institute,
Houston, Texas.

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[1] Scott and Durham: J. Phys. Chem., **34**, 2035 (1930).

THE DISSOCIATION PRESSURES OF HYDRATED CUPRIC SULFATE AT 35 DEGREES CENTIGRADE[1]

BY THOMAS S. LOGAN

The dissociation pressures developed by the hydrates of cupric sulfate have been the subject of a number of investigations.[2] Such work has, however, usually been carried out as merely one of a series of determinations involving several salts. The data available at $25°$ have been tabulated by Wilson,[3] who has pointed out that they are not at all concordant. In the case of hydrated cupric sulfate, the following values at $35°$ have been published:

$$CuSO_4.3-5 \ H_2O \ 17^{2a}, \ 15.6^{2d}, \ 16.5^{2e}, \ 17.01^{2f}$$
$$CuSO_4.1-3 \ H_2O \ 7.5^{2a}, \ 11.8^{2e}$$
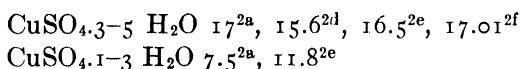
The values are in millimeters of mercury. No records of measurements on $CuSO_4.0-1 \ H_2O$ at this temperature have been found.

The extreme slowness with which the hydrates of cupric sulfate establish equilibrium pressure has occasioned some comment. Carpenter and Jette[2c] include in their data curves showing that in the case of a mixture of the penta- and tri-hydrates, equilibrium was established from either side only after fourteen days. The influence of small amounts of air on the establishment of true equilibrium has been shown by Patrick and MacGavack.[4] Menzies[2g] discusses this point and describes an experiment whereby he shows that such accumulated air is due to an adsorbed layer on the cupric sulfate which is persistently held.

The purpose of the present work was to prepare a sample of cupric sulfate pentahydrate under air-free conditions, to withdraw the water in successive portions, taking pressure measurements after each withdrawal, and thus to find out how air-free conditions influenced the time required to establish equilibrium.

Apparatus

An outline of the glass apparatus used is shown in Fig. 1. The hydrated salt was contained in the bulb, A, connected directly to one arm of the manometer. The traps marked a were found necessary to prevent the flowing out of the very fine powder obtained when cupric sulfate is dehydrated. Any powder depositing here could be washed down by condensing water above. The plug, b, made it possible to trap off the hydrate if it was necessary to admit the

[1] From the dissertation submitted by T. S. Logan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Lescoeur: Ann. Chim. Phys. (6), 21, 511 (1890); Andreae: Z. physik. Chem., 7, 241 (1891); Foote and Scholes: J. Am. Chem. Soc., 33, 1309 (1911); Frowein: Z. physik. Chem., 1, 5 (1887); Carpenter and Jette: J. Am. Chem. Soc., 45, 578 (1923); Partington: J. Chem. Soc., 123, 160 (1923); Menzies: J. Am. Chem. Soc., 42, 1951 (1920); Schumb: J. Am. Chem. Soc., 45, 342 (1923).

[3] Wilson: J. Am. Chem. Soc., 43, 704 (1921).

[4] Patrick and MacGavack: J. Am. Chem. Soc., 42, 946 (1920).

atmosphere to the system. The arms of the manometer, B, were constructed of tubing with an inside diameter of 12 millimeters. At the base these were run into an air trap which was connected to a length of 1.5 millimeter capillary tubing, sealed through the stopcock, c, to the mercury reservoir, d. This construction was all glass, in order to eliminate any fouling of the mercury by rubber. The height of mercury in the manometer could be regulated by connecting the outlet of the mercury reservoir to a pump.
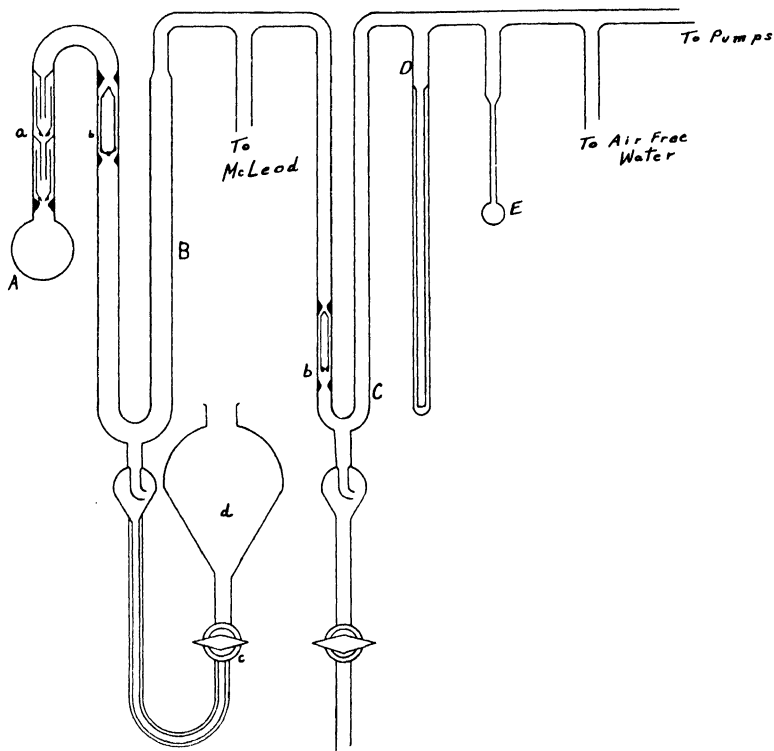
FIG. 1

A McLeod gage was sealed into the manifold as indicated. This was of the type suggested by Taylor.[5] The readings of permanent gas as taken here, when the manometer was drawn down to permit diffusion, could be converted to the actual pressure in the hydrate bulb through a knowledge of the volume ratio involved. In this apparatus this was approximately 5 to 1.

The trap, C, containing another of the plugs, b, served to trap off the system while measurements were being made, in case it was necessary to admit the atmosphere.

A piece of capillary tubing of known cross-section was sealed in at D. By surrounding this with ice it was possible to condense here the approximate amounts of water it was desired to introduce into or remove from the salt.

[5] Taylor: J. Am. Chem. Soc., 50, 2937 (1928).

In such cases exact determination was made by then condensing the water in the bulb, E, which was sealed off and weighed. The apparatus had a cluster of six or eight bulbs here, instead of one as illustrated, which could be replaced as desired by raising the proper traps.

The apparatus as indicated was connected to a system of pumps and to a reservoir of air-free water. The McLeod gage, the bulb of hydrate, the manometer, and the trap, C, were all immersed in the water of a thermostat, the mercury leads extending through the bottom to atmospheric height. At $35°$ the temperature variation of the thermostat was $0.005°$. The temperature was read off a Beckmann thermometer which was calibrated against a thermometer certified by the Bureau of Standards. The latter had scale divisions of $0.01°$.

The measurements of the pressure were taken by means of a cathetometer, using a millimeter scale set in brass.

The mercury used was cleaned by running it in a thin stream successively through 1500 centimeter columns of dilute nitric acid and distilled water. It was then distilled in vacuo.

The cupric sulfate used was Baker's C. P. recrystallized a number of times from distilled water.

Approximately 12 grams of the pentahydrate of cupric sulfate was used for each sample in the experiments described.

Deaeration

Preliminary experiments on eliminating air showed that it was possible to get the salt in a condition where the amount of permanent gas in the vapor phase was very small, while there was still a considerable amount retained by the solid. The final procedure adopted for deaeration was as follows. The weighed sample of the pentahydrate of cupric sulfate was placed in the bulb, A, and the system was pumped out as far as possible. The treatment of the salt was essentially a succession of hydrations and dehydrations. The pentahydrate was heated at $250°$, the water being pumped out as it appeared, until the pressure above the salt remained constant at 10^{-4} millimeter, when dehydration was considered complete. According to Krafft[6] hydrated cupric sulfate loses its water in vacuo completely at $250°C$. The salt was then rehydrated by opening to air-free water while the bulb was surrounded by ice. The dehydration was then repeated.

At first the salt was hydrated completely before each withdrawal of water. However, a series of experiments showed that the greatest part of the permanent gases appeared only during the loss of the last mol or so of water, that is, when heating from $150°$ to $250°$. For this reason complete hydration was discontinued. During the latter part of the process the anhydrous salt at room temperature was thrown in contact with the reservoir of air-free water and allowed to hydrate over a period of from two to four hours. The manifold was then trapped, after being tested for air-free conditions; the salt was left open to the manifold. The temperature around the bulb of cupric sulfate was raised slowly to $250°$, the water driven off condensing in the manifold. When

[6] Krafft: Ber., **40**, 4770 (1907).

the outflow of water had ceased, the vapor above the liquid water in the manifold was examined for air. The water in the manifold was then pumped out and the whole system, including the bulb of salt at 250°, was pumped down to 10^{-4} millimeter. The pumping was maintained at this pressure for two or three hours.

Such a succession of operations was run on the cupric sulfate for periods of from two to three weeks. When the amount of air appearing in the manifold at the end of a dehydration was of the order of 5×10^{-4} to 10^{-3} millimeter conditions were considered as satisfactory for undertaking measurements.

The Measurements

Measurements of dissociation pressure above the systems $CuSO_4.5H_2O$— $CuSO_4.3H_2O$ and $CuSO_4.3H_2O$—$CuSO_4.H_2O$. The pentahydrate of cupric sulfate was taken as the starting point for the measurements. This was secured by condensing successive portions of air-free water on the salt, after determining the amount of this water by condensing it first in the capillary, D, Fig. 1. Sufficient water was run in on the salt to insure an excess above that equivalent to five mols per mol of cupric sulfate.

The salt was left standing for four days in contact with this excess water to insure complete hydration and also with the view of seeing how permanent gas accumulated during this time. In four days approximately 1.5×10^{-4} millimeter of air appeared in the manifold. During this period parts of the system had been as hot as 70° due to work with the thermostat. It was thought that a good portion of this air might have come out of the glass walls.

The pentahydrate was finally secured by having the bath around the bulb of salt and excess water regulating at 35°. The dissociation pressure of the hydrate at this temperature is 16.4 millimeters. The vapor pressure of a saturated solution of cupric sulfate at 35° is about 33 millimeters. The room temperature was around 26°. By leaving the trap, C, open, it is clear that distillation of any water in the bulb would occur into the manifold at room temperature. The vapor pressure of the condensed water would prevent the dissociation of any hydrate.

When obtained, the pentahydrate was warmed until the desired amount of water was lost, this being condensed in the capillary, D, and then in a small bulb which was sealed off and weighed. The method of simply heating the hydrate to drive out water had to be subjected to further control. Several methods were attempted. The one finally adopted consisted in heating the hydrate to such a temperature that its dissociation pressure was in excess of the vapor pressure of water at the temperature of the manifold. The water would then condense in the manifold as it was lost by the hydrate. The amount to be withdrawn was condensed in a bulb, sealed off, and weighed. The temperature of the hydrate was then lowered to such an extent that the vapor pressure of the water remaining in the manifold was in excess of the dissociation pressure of the particular hydrate pair desired. That is, in working with the system $CuSO_4.3H_2O$—$CuSO_4.H_2O$, conditions were so adjusted that there could be no formation of $CuSO_4.5H_2O$.
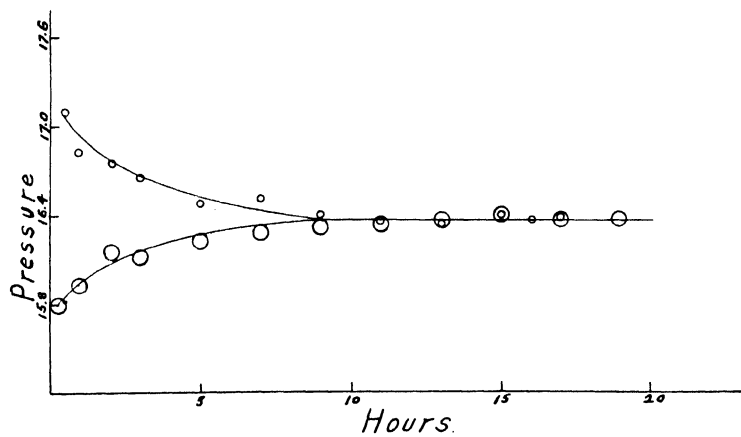
FIG. 2
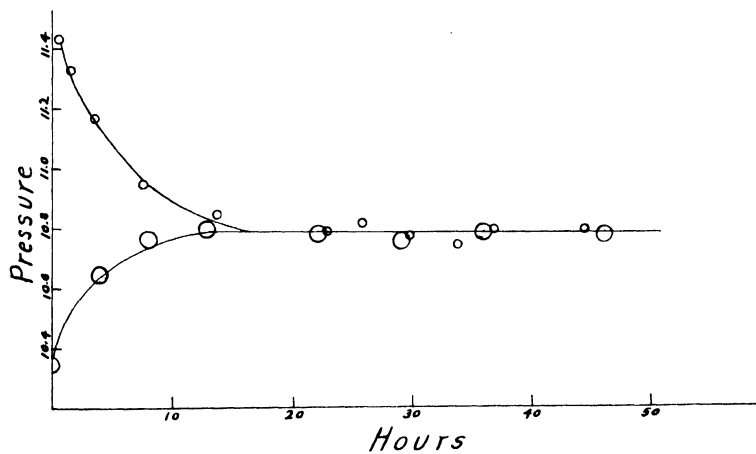
FIG. 3
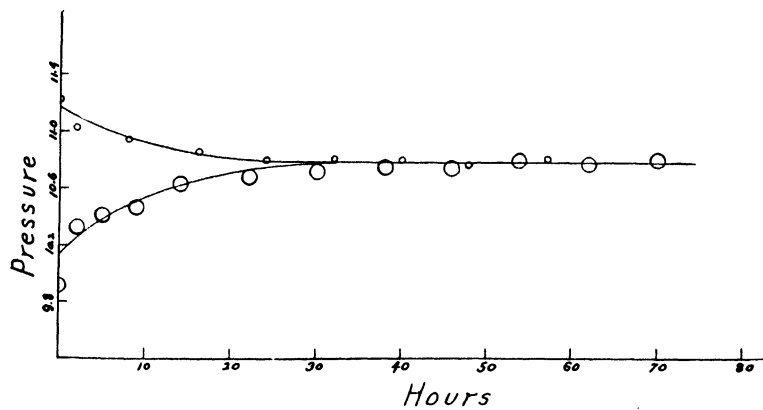
FIG. 4

The same considerations were applied in driving water out. This process of partial hydration and dehydration was repeated two or three times. The measurements available in the literature were used in making the adjustments. The pentahydrate was not reformed after each measurement. The additional water necessary to alter the water content as desired was withdrawn.

Measurements from the high pressure side were obtained by introducing a pressure of water vapor into the manifold in the desired excess over that in the hydrate bulb. The manometer was then drawn down until the hydrate was open to this excess, the trap, C, being raised. By such an operation the excess

TABLE I

Summary of Measurement 3
Composition $CuSO_4 . 3.67 H_2O$
Temperature $35° \pm 0.005$

a. Excess pressure of 9 millimeters expanded onto hydrate		b. Excess pressure of 7 millimeters in hydrate bulb expanded into manifold	
Time	Pressure	Time	Pressure
0.0 Hours	18.35 mm.	0.0 Hours	15.13 mm.
0.5 ″	17.10 ″	0.3 ″	15.80 ″
1.0 ″	16.83 ″	1.0 ″	15.93 ″
2.0 ″	16.76 ″	2.0 ″	16.17 ″
3.0 ″	16.65 ″	3.0 ″	16.13 ″
5.0 ″	16.48 ″	5.0 ″	16.24 ″
7.0 ″	16.52 ″	7.0 ″	16.30 ″
9.0 ″	16.41 ″	9.0 ″	16.33 ″
11.0 ″	16.38 ″	11.0 ″	16.35 ″
13.0 ″	16.36 ″	13.0 ″	16.38 ″
15.0 ″	16.42 ″	15.0 ″	16.42 ″
16.0 ″	16.38 ″	17.0 ″	16.39 ″
17.0 ″	16.40 ″	19.0 ″	16.39 ″
Mean 16.39 ″		Mean 16.38 ″	

pressure expanded into the lower pressure side, initially assuming four-fifths of what it was before expansion. After such expansion the mercury in the manometer was allowed to rise to the desired height. This procedure was simply reversed in following a rising pressure. The type of results obtained and the time required for equilibrium to be reached are best illustrated by the detailed sets of data shown in Tables I, II, and III. Curves for these measurements are shown in Figs. 2–4.

The time marked zero time in the tables represents a lapse of about ten minutes from the time of actually trapping off the hydrate under its initial pressure, this being the time necessary to pump the system down to 10^{-4} millimeter. The pressures are recorded in millimeters of mercury at $35°$. Each is the mean of from two to four cathetometer settings in which the maximum deviation from the mean never exceeded 0.02 millimeter.

TABLE II

Summary of Measurement 5

Composition $CuSO_4 . 2.69 H_2O$

Temperature $35° \pm 0.005$

a. Excess pressure of 5 millimeters expanded onto hydrate		b. Salt warmed up from 26°. First reading taken at 35°	
Time	Pressure	Time	Pressure
0.0 Hours	11.86 mm.	0.0 Hours	10.35 mm.
0.3 ”	11.43 ”	4.0 ”	10.65 ”
1.3 ”	11.33 ”	8.0 ”	10.76 ”
3.3 ”	11.17 ”	13.0 ”	10.80 ”
7.3 ”	10.95 ”	22.0 ”	10.78 ”
14.3 ”	10.85 ”	29.0 ”	10.76 ”
23.3 ”	10.79 ”	36.0 ”	10.79 ”
26.3 ”	10.82 ”	46.0 ”	10.79 ”
30.3 ”	10.78 ”		Mean 10.78 ”
34.3 ”	10.75		
37.6 ”	10.80		
47.0 ”	10.79		
Mean 10.79 ”			

TABLE III[7]

Summary of Measurement 8

Composition $CuSO_4 . 1.09 H_2O$

Temperature $35° \pm 0.005$

a. Time	Pressure	b. Time	Pressure
0.0 Hours	11.22 mm.	0.0 Hours	9.92 mm.
2.0 ”	11.03 ”	2.0 ”	10.33 ”
8.0 ”	10.95 ”	5.0 ”	10.41 ”
16.0 ”	10.86 ”	9.0 ”	10.47 ”
24.0 ”	10.81 ”	14.0 ”	10.64 ”
32.0 ”	10.82 ”	22.0 ”	10.69 ”
40.0 ”	10.81 ”	30.0 ”	10.73 ”
48.0 ”	10.78 ”	38.0 ”	10.77 ”
57.0 ”	10.82 ”	46.0 ”	10.76 ”
Mean 10.81 ”		54.0 ”	10.81 ”
		62.0 ”	10.78 ”
		70.0 ”	10.81 ”
		Mean 10.78 ”	

[7] This measurement was obtained from a different sample of cupric sulfate. This is discussed in the summary.

Measurements on the system $CuSO_4.H_2O—CuSO_4$. The variation of water content was brought about differently to obtain these measurements. On the first trials the cupric sulfate was completely dehydrated. An amount of water corresponding to 0.1 mol was condensed in the capillary, D. This was surrounded with ice. The dehydrated salt at a temperature of 35° was put in contact with this water. The pressure of the water vapor was thus such as to eliminate the possibility of any formation of trihydrate. The water was determined by condensing the same amount into a bulb and weighing.

A measurement was obtained on this mixture of monohydrate and anhydrous salt and then additional water was run in as already described above, the process being repeated until three measurements were obtained. These

<div align="center">

TABLE IV

Duration of Heating	Temperature	Mean Pressure
5 Days	100°–110°	0.31 mm.
5 ”	”	0.21 ”
6 ”	”	0.17 ”
3 ”	”	0.17 ”

</div>

showed a rising pressure as the water content increased. It was thought that this variation might be due to adsorbed water building up a pressure in excess of the dissociation pressure of the system. The reversion to the monohydrate would then be exceedingly slow at 35°, as indicated by the fact that the measurements obtained held constant over considerable periods of time.

The measurements were accordingly repeated. In this repetition the hydration was carried out as outlined above except that the salt was kept at a much higher temperature. Such temperature was maintained for several days after the water had been taken up. The salt was then cooled down slowly and a measurement obtained at 35°. Then the heating was resumed for a period, after which another measurement at 35° was made. This was continued until the measurements obtained after such periods of heating checked. For the two measurements on the monohydrate at the lower water content, the temperature of heating was 100° to 110°. With the higher water content it was necessary to heat at 140° to 150° in order to get equilibrium in any reasonable length of time.

The general course of the measurements is illustrated by Table IV which shows a summary of the measurement on $CuSO_4.0.126\,H_2O$.

In obtaining the mean pressures recorded above and also in the final summary, measurements were run from both sides of equilibrium. To measure a rise from the lower side, the pressure above the hydrate, 0.18 mm., was allowed to expand into the manifold, the manometer was raised and the system pumped out. By the time pressure readings could be taken they were, within the limits of error, 0.18 mm.

Measurements were also taken with a dropping pressure, but here the change was much more gradual and was such as to indicate that a rather large initial pressure resulted in some adsorption. For this reason the excess pressure allowed to expand onto the salt was usually 1 to 2 millimeters. This dropped to the equilibrium value in the course of 6 to 12 hours.

Results

A summary of the measurements obtained is shown in Table V. The measurements evidently establish the existence of the penta-, tri-, and mono- hydrates of cupric sulfate.

The measurements are plotted in Fig. 5.
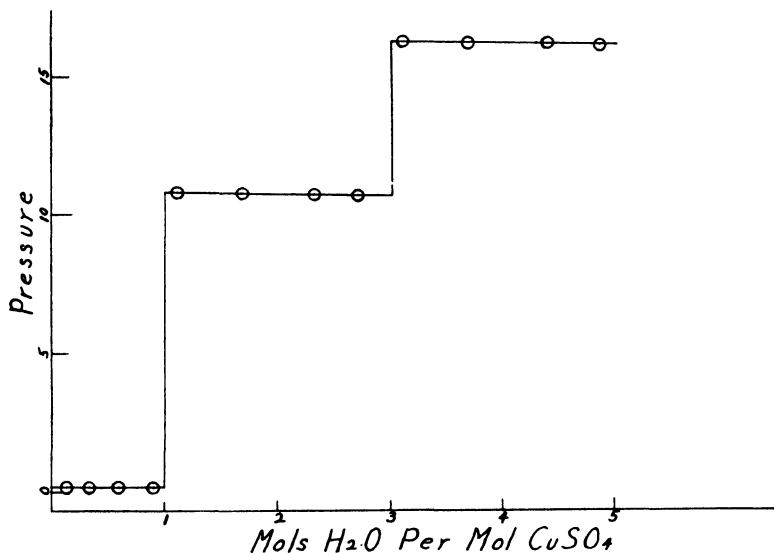
FIG. 5

TABLE V

Number	Composition	Mean Pressure
1	$CuSO_4. 4.84 H_2O$	16.39 mm.
2	$CuSO_4. 4.41 H_2O$	16.40 "
3	$CuSO_4. 3.67 H_2O$	16.39 "
4	$CuSO_4. 3.10 H_2O$	16.42 "
5	$CuSO_4. 2.69 H_2O$	10.79 "
6	$CuSO_4. 2.32 H_2O$	10.80 "
7	$CuSO_4. 1.68 H_2O$	10.80 "
8	$CuSO_4. 1.09 H_2O$	10.80 "
9	$CuSO_4. 0.91 H_2O$	0.17 "
10	$CuSO_4. 0.59 H_2O$	0.18 "
11	$CuSO_4. 0.34 H_2O$	0.18 "
12	$CuSO_4. 0.13 H_2O$	0.17 "

In obtaining these results, two samples of cupric sulfate were used. The first seven measurements were obtained with the first sample, the last five with the second. During the course of the experiments on the first sample, breaks in the apparatus admitted air on two occasions. This required that the process of deaeration be repeated twice after the first time. Measurements 1 and 6 were obtained after the first deaeration; 2, 3, and 4 after the second; 5 and 7 after the third. After Measurement 7 was obtained the salt

was accidentally heated to a temperature of about 325°. Some decomposition occurred and it was found to be unsuitable for further work. It was accordingly discarded.

In working with the second sample it was found that heating to about 110° and at the last to 150° caused the loss of four mols of water, and that then it was possible to pump the system down to 10^{-4} millimeter while keeping the salt at a temperature of 100°. Over a period of four hours this pressure increased to about 2×10^{-3} with no pumping and the amount of permanent gas present was very small. This was considered as indicative that air-free conditions could be maintained at a lower temperature and a higher water content.

The salt was hydrated completely and enough water withdrawn to insure its being a mixture of the two higher hydrates. Two measurements were then obtained at 35,° one from each side of equilibrium. The values were 16.38 and 16.40 millimeters. The salt was then subjected to treatment previously outlined to reduce its composition to $CuSO_4$. $1.09 H_2O$.

Measurement 8 was thus obtained without removal of such deep-seated air as had been taken out in the previous cases. Such a course of complete deaeration was however gone through, before the measurements on the monohydrate were taken. At the end of these measurements the salt was again hydrated completely and then brought to a composition of about $CuSO_4$. $4.5 H_2O$. A measurement of the dissociation pressure at 35° was in satisfactory accord with those obtained earlier.

At the end of each measurement the water vapor above the hydrated salt was examined for permanent gas. In no case did the partial pressure of this exceed 2×10^{-3} millimeter, and in most cases it was considerably less than this. The data tabulated have shown that the absence of permanent gas has a very marked effect on the time required for equilibrium to be reached. In the case of the highest hydrate pair equilibrium was reached with considerable rapidity—about an hour as compared with much longer periods mentioned elsewhere. In the case of the lower pairs the process is slower, but still fairly rapid.

Summary

1. An apparatus is described for the determination of the dissociation pressures of hydrated salts by the statical method.

2. A method for eliminating adsorbed air from such hydrates is described.

3. The 35° isotherm for the dissociation pressures of cupric sulfate containing a varying amount of water of hydration has been determined under air-free conditions.

4. The measurements obtained indicate the existence of $CuSO_4.5H_2O$, $CuSO_4.3H_2O$, and $CuSO_4.H_2O$.

Acknowledgment

The Johns Hopkins University,
Baltimore, Maryland.

TRANSFERENCE NUMBER OF COBALT SULFATE*

BY R. C. CANTELO AND E. C. PAYNE[1]

This paper records the results of an investigation which was undertaken to determine how the transference number of cobalt sulfate varies with the concentration of the solution.

A review of the literature indicates that no data exist for the transference number of cobalt sulfate. In fact, the only such investigations on cobalt salts are those of Bein[2] for cobalt chloride, and of Denham[3] for cobalt bromide. Bein gives only one value, $T_{Cl}^- = 0.596$ for a concentration corresponding to 0.199 per cent chlorine. Denham's results are given in Table I.

TABLE I

Cobalt Bromide Solutions

Conc'n. moles per liter	0.090	0.459	1.345	2.448	3.106	4.731	5.554
T_{Co}^{++}	+0.409	0.413	0.340	0.322	0.215	0.005	−0.444

Denham explained these decreasing and negative values by assuming the formation of "auto-complexes" such as $CoBr_3^-$ and $CoBr_4^=$ which transfer cobalt towards the anode.

With respect to these kinds of phenomena McBain and Van Rysselberghe[4] have shown that a common ion, when added in large excess, to the solution of a bivalent cation (and to less extent for univalent cations), will suppress the movement of that ion towards the cathode, and may even reverse its direction, causing it to show a negative transference. Further, they have shown that these phenomena likewise occur with very concentrated solutions of a single salt. They say:

"If complexes occur in mixtures of two salts, they must also occur in solutions of one salt of the same (anion) concentration. From the mass action principle, even greater amounts of the complexes will be formed, but less in proportion to the total salt present."

McBain and Van Rysselberghe have attempted to show that these results are "incompatible with any complete dissociation theory," since they believe it to be necessary for complex formation: that the simple anion combine with the undissociated molecule to form the complex ion.

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* Contribution from the Department of Chemistry, College of Liberal Arts, University of Cincinnati.

[1] An abstract of a part of the dissertation presented by E. C. Payne to the Graduate School, University of Cincinnati; in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Bein: Z. physik. Chem., 27, 1 (1898).

[3] Denham: Z. physik. Chem., 65, 641 (1909).

[4] McBain and Van Rysselberghe: J. Am. Chem. Soc., 50, 3009 (1928); 52, 2336 (1930).

Materials

Cobalt Sulfate.—The cobalt sulfate was the so-called C.P. grade which originally contained one per cent nickel as nickel sulfate. It was purified in two ways, each of which gave an apparently pure product. The first method was that used by Cantelo and Berger[1] in their work on the electrical conductance of cobalt sulfate. The second method of purification was based on that described in "U. S. Bureau of Mines Information Circular 6331."

Cobalt Sulfate Solutions.—Conductivity water was used in the preparation of all solutions; the solutions were made up fresh for each determination.

Analytical Method

All analyses were made by electrolysis. The method was essentially that described by Lundell and Hoffmann,[2] but certain modifications were used. A portion of solution was taken for analysis which contained from 0.15 to 0.25 grams of cobalt. To this was added a mixed solution containing the equivalent of 10 cc. concentrated sulfuric acid and 55 cc. of strong ammonia. The solution was made up to 150 cc. and was electrolyzed for 1-½ hours, with a current of 0.6 to 1 ampere and a voltage of 2.5 to 3.5. A cylindrical cathode of platinum gauze and a rotating platinum spiral anode were used. At the end of one hour, or when the solution became colorless, the cover glass and the sides of the beaker were washed down and about 0.5 gram of sodium bisulfite was added. The sodium bilsulfite aids apparently in the deposition of the last portion of cobalt, but tends to form small amounts of sulfide on the cathode.

It was found inadvisable to remove all the cobalt by electrolysis as platinum may be plated onto the cathode. Accordingly, after 1-½ hours of electrolysis, the residue was precipitated by ammonium sulfide, after the excess ammonia had been removed by boiling. The cobalt sulfide was filtered, washed with water containing ammonium chloride and ammonium sulfide, ignited and weighed. The weight of oxide so obtained, seldom more than 1 milligram, was multiplied by an empirical factor, ¾, and the result, (as cobalt) was added to the weight of cobalt deposited on the cathode.

Apparatus

In this investigation, we have tried to follow the suggestions given by Noyes and Falk,[3] namely:

1. "Both cathode and anode portions should be analyzed." This was done, but the anode portion did not give reliable results.

2. "The change in concentration should be as large as possible."

3. "It is advisable to analyze three middle portions."

4. "The character of the electrodes should be such as to form no migrating substance likely to cause error in analysis."

5. "Apparatus should be so designed as not to cause convection currents and stirring, during electrolysis and removal of the solution."

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[1] Cantelo and Berger: J. Am. Chem. Soc., **52**, 2648 (1930).

[2] Lundell and Hoffman: Ind. Eng. Chem., **13**, 540 (1921).

[3] Noyes and Falk: J. Am. Chem. Soc., **33**, 1436 (1911).

The apparatus used was essentially that of A. A. Noyes.[1] The inside diameter was 23 mm. and was uniform throughout. The total distance between the electrodes was about 70 cm. The apparatus was made in two parts, and joined at the middle by rubber tubing, wired tight, and coated with ceresine wax.

Several electrodes were tried but the only satisfactory ones were: a cathode of very fine platinum gauze, and an anode of similar material plated with cobalt. These electrodes were flat circular pieces of gauze about 1-1/4 cm. in diameter. They were welded to pieces of platinum wire, which were sealed into the end of a 6 cm. length of 4 mm. glass tubing. On the inside of the tube contact was made with a copper wire by means of Wood's metal. This tube, joining the electrode, was joined to a longer one by means of rubber tubing; and the longer one was held in place at the top of the transference apparatus by passing through a rubber stopper. Electrical connection was made by means of a copper wire which passed through the long tube and was connected to the wire in the short one by means of a loop and hook. The electrode end, thus, could be detached and weighed.

The gauze cathode left nothing to be desired. The number of equivalents of cobalt plated on it in an experiment checked very well with the amount calculated from the silver coulometer. The anode, however, did not dissolve, on electrolysis, with any degree of regularity, and consequently, few of the anode portions could be checked against the cathode portions. After electrolysis the anode was coated with a material which was, apparently, an oxide. This oxide varied in color from pink, blue or green to brown. Some of this material fell to the bottom of the anode compartment as a sludge.

Current was measured by a silver coulometer which was constructed as follows: The cathode was a deep platinum dish of about 200 cc. capacity; the anode was a bar of pure silver, coated with electrolytic silver and wrapped in ashless filter paper. The silver nitrate was purified by the method of Rosa and Vinal.[2] Current was indicated roughly by a milliammeter, and the strength of current was adjusted by a slide-wire resistance.

Experimental Procedure

The two halves of the apparatus were cleaned and dried; and were joined as described previously, and the solution was poured into the completed cell. The levels were adjusted to 3-4 cm. above the bends in the outer arms, and the small withdrawal tubes were stoppered. The electrodes were then inserted and adjusted so as to be just below the surface of the solution. The anode had been weighed previously. The apparatus was immersed almost to the top of the withdrawal tubes in a thermostat kept at the temperature $25°\pm0.02$. After at least thirty minutes the current was applied at a sufficiently high voltage to pass the desired current, 5 to 80 milliamperes. Since storage cells were used as the source of electricity, the current could be kept very constant.

[1] A. A. Noyes: J. Am. Chem. Soc., **23**, 42 (1901).
[2] Rosa and Vinal: Bur. Standards, Bull., **13**, 479 (1916-17).

Current was passed for as long a time as, as found by experience, would give the maximum change in concentration about the electrodes, without changing the concentration of the middle portions. This time varied from 3 to 12 hours with 4 to 6 hours as the most usual.

After the current was stopped, the solution was separated into five parts. The middle portion (M), and the two adjacent portions, (AM and CM), in the vertical arms of the tube, were carefully pipetted directly into dried and weighed flasks by means of suction. The tip of the pipette was kept just below the surface of the solution to avoid stirring.

The two electrodes were removed and carefully rinsed with a very small amount of the original solution into their respective compartments. They were then rinsed with water, dried and weighed. The cathode deposit was dissolved in nitric acid, again dried and weighed, and the weight of the cobalt deposit was determined.

The coulometer was emptied, carefully rinsed, dried and weighed and the weight of the silver deposited was taken as a measure of the current passed. As has been mentioned previously, there was good agreement between the number of equivalents of silver deposited, and the number of equivalents of cobalt deposited on the cathode.

The two halves of the apparatus were separated and stoppered. The exterior of the glass was wiped off and the apparatus and contents weighed. The solutions were well mixed, poured out into dry flasks, and the tubes were rinsed, dried and weighed.

The five portions were analyzed electrolytically and the transfer of the cobalt sulfate was calculated. As has been mentioned above, the anode results were unreliable.

Results

Table II contains the transference numbers of cobalt calculated from the change in concentration of the cathode portion.

TABLE II

Transference Numbers of Cobalt Sulfate Solutions

Concn. N	Faradays passed	Equivalents lost by Cathode middle	Cathode	Transference No. of Co++
3.994	0.006627	0.00	0.005640	0.149
3.104	0.005624	0.00002	0.004320	0.232
2.833	0.010504	0.00	0.007776	0.260
2.331	0.003335	0.000121	0.002408	0.278
1.860	0.008620	0.000025	0.006154	0.286
1.454	0.003176	0.00	0.002195	0.309
1.444	0.002632	0.00	0.001801	0.316
0.996	0.007536	0.000103	0.004850	0.356
0.753	0.002550	0.00	0.001854	0.373
0.473	0.002929	0.00	0.001787	0.390
0.233	0.002610	0.00	0.001577	0.396

Discussion of Results

Cantelo and Berger[1] found for the equivalent conductance of cobalt sulfate at zero concentration the value $\Lambda_o = 134.6$ mhos for $25°$. The ion-conductance of SO_4^- at $25°$ is 78.4. Hence the transference mumber of Co^{++} in cobalt sulfate is $56.2/134.6 = 0.419$ for solutions of zero concentration.

An examination of Table II shows at once how greatly the determined transference numbers deviate from the value calculated for zero concentration. The measured values vary from 0.396 for a 0.233 N solution to 0.149 for a 3.994 normal solution.

These results indicate that with increasing concentration, either there is a *very great change in the ratio of the mobilities* of the cobalt and sulfate ions or that there is the appearance of complex ions in increasing concentration as the solutions increase in stoichiometrical concentration.

If we consider that the rapid increase in the transference numbers with increasing concentration is due to a change in the ratio of the ion mobilities, we can find a possible explanation in excessive hydration of cobalt ion.[2] It is necessary to assume that the cobalt ion is more highly hydrated than the sulfate ion. Suppose that each Co^{++} ion carries ten molecules of bound water more than the anion. During transference this water is carried to the cathode, thereby displacing the whole solution towards the anode. Then for one Faraday carried by Co^{++}, there would be an apparent movement towards the anode of 5 moles or 90 grams of water. For 0.233 N cobalt sulfate solution, this would give $0.233 \times 0.09 = 0.021$ equivalents change in the apparent migration. But this is further reduced, if we use the value for T_{Co}^{++} for zero concentration to $0.021 \times 0.42 = 0.009$ equivalents for the total effect on the migration. The actual change in migration is $0.419 - 0.396 = 0.025$. This method of explanation is, therefore, inadequate to explain our results. A correction two and one-half times greater would be required to explain them in this way. For the 3.994 N solution, the change in the apparent migration due to 10 molecules of water of hydration would be $3.994 \times 0.09 \times 42 = 0.151$ equivalents. Actually the change in migration is $0.419 - 0.151 = 0.268$ equivalents, a value nearly twice as great. Such great hydration seems very improbable.

The second explanation lies in the admission that we are dealing here with complex ions, such as $Co(SO_4)_2^=$. Pfanhauser[3] found that in a saturated solution of nickel ammonium sulfate, the nickel moves entirely to the anode in the form of the complex ion, $Ni(SO_4)_2^=$. Thus, it seems probable that such complex ions exist in solutions of cobalt sulfate. The decreasing values of the tranference numbers of Co^{++} are due to the increasing amounts of cobalt carried to the anode as complex ions.

[1] Cantelo and Berger: loc. cit.
[2] See McBain and Van Rysselberghe: J. Am. Chem. Soc., 50, 3016 (1928).
[3] Pfanhauser: Z. Elektrochemie, 7, 698 (1901).

Summary

The transference number of cobalt ion in cobalt sulfate solutions at concentrations 0.233 to 3.994 N has been measured at 25°.

In this range the transference number varies from 0.396 to 0.149. The value calculated from the ion conductance is 0.419.

It has been shown that the assumption of excessive hydration of the cobalt cation is inadequate to explain the deviations of the T_c values from 0.419.

It has been suggested that the admission of complex anions of the type $Co(\overline{SO_4})_2$ etc., affords a much more logical explanation.

Cincinnati, Ohio.

THE THEORY OF GASEOUS EXPLOSIONS AND THE OXIDATION OF HYDROGEN SULPHIDE

BY H. AUSTIN TAYLOR

H. W. Thompson[1] in a paper under the above title has recently criticised the results of some investigations upon the oxidation of hydrogen sulphide[2] and of ethane[3] considered from the point of view of the theory of gaseous explosions developed by Semenoff. It is claimed that the use of the Semenoff results in the form of an equation:

$$\log p = A/T + B$$

instead of:

$$\log p/T = A/T + B$$

has "invalidated much of the interpretation of the results of the oxidation of hydrogen sulphide" while at the same time it is admitted that precisely the same conclusions would have been drawn had the second equation been used, as were drawn from the results of the first equation.

It is the object of the present paper to show that both equations are approximations of a more general equation and while it must be admitted that the log p/T form is the more accurate, due to a fortuitous cancellation of errors, the value of A which it yields is higher than the true value. The employment of the log p equation can hardly therefore be judged as a "misunderstanding of the essential results of Semenoff's theory." It is hoped further to show that other criticisms are unwarranted on the basis of the evidence presented.

In order to demonstrate this it will be necessary to consider the Semenoff theory in detail and enumerate the many approximations that are involved in the deduction of the final expression in either of the above forms. The actual magnitude of these approximations has not yet apparently been considered even by Semenoff.

Semenoff's theory of thermal explosions with which we are concerned here assumes a production of heat, by reaction between molecules activated in the "classical Arrhenius" sense, at a rate which is greater than that of the loss of heat by conduction, or by radiation from the walls.

Considering a mixture of a molecules of type A and b molecules of type B the rate of reaction is proportional to $a\,b\,e^{-E/RT}$ where E is the energy of activation. The rate of production of heat by the reaction assumed exothermal is then given by:

$$q_1 = B\,a\,b\,e^{-E/RT} \tag{1}$$

where B is a constant involving the heat of reaction, size of vessel, collision

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[1] J. Phys. Chem., **35**, 3639 (1931).

[2] Taylor and Livingston: J. Phys. Chem., **35**, 2676 (1931).

[3] Taylor and Riblett: J. Phys. Chem., **35**, 2667 (1931).

frequency and so on. The rate of loss of heat by the system is supposed as a first approximation to be proportional to the temperature difference between the reacting mixture and the walls, that is:

$$q_2 = k(T - T_o) \tag{2}$$

where T is the temperature of the reacting gases and T_o that of the walls of the containing vessel. In the limiting case for explosion the rate of production of heat equals the rate of loss of heat and the rates of change of each of these with temperature must be equal. For a gas mixture entering a vessel at T_o and exploding at a temperature T_2 we have:

$$B \, a \, b \, e^{-E/RT_2} = k(T_2 - T_o) \tag{4}$$

and

$$B \, a \, b \, e^{-E/RT_2} = k(RT_2^2/E) \tag{5}$$

whence

$$T_2 - T_o = RT_2^2/E \tag{6}$$

and

$$T_2 = E/2R \cdot (1 \pm \sqrt{1 - 4RT_o/E})$$

The positive sign before the root would make T_2 so much greater than T_o as to be impossible. Hence we may take:

$$T_2 = E/2R \cdot (1 - \sqrt{1 - 4RT_o/E}) \tag{7}$$

From (5) substituting this value of T_2 we have

$$B \, a \, b \, \exp\left(-\frac{2}{1 - \sqrt{1 - 4RT_o/E}}\right) = k \, E/4R \cdot (1 - \sqrt{1 - 4RT_o/E})^2$$

If n is the total number of molecules and α is the fraction of type A then $a = \alpha n$ and $b = (1 - \alpha)n$. If n_o is the number of molecules in the vessel at N.T.P. and δ and δ_o the densities under reaction conditions and N.T.P. respectively then $n = n_o \delta / \delta_o$ where $\delta_o = 760/R273$ and $\delta = p/RT_o$, p being the observed pressure of the gas mixture. Making these substitutions and taking logarithms we obtain:

$$\ln p/T_o = 1/(1 - \sqrt{1 - 4RT_o/E}) + \ln E^{1/2} (1 - \sqrt{1 - 4RT_o/E}) + K \quad (8)$$

where K is a constant involving B, n_o, α etc., that is, a constant for a given reaction mixture.

This is the exact form of the equation which Semenoff's theory yields before any immediate approximations are included. The principal approximation made in an attempt to simplify the above equation is that $\sqrt{1 - 4RT_o/E} = 1 - 2RT_o/E$. That this approximation is not justifiable can be seen by referring to equation (7) where

$$T_2 = E/2R \cdot (1 - \sqrt{1 - 4RT_o/E})$$

which with the approximation becomes $T_2 = T_o$ indicating either no reaction or reaction with no heat change, in neither of which cases could explosion possibly occur. Overlooking this momentarily however if we assume this approximation and introduce it into the general equation (8) we obtain:

$$\ln p/T_o = E/2RT_o + \ln 2RT_o/E^{1/2} + K \tag{9}$$

and assuming with Semenoff that $\ln T_o$ does not change much in the average temperature range studied, the expression may be written:

$$\ln p/T_o = A/T_o + B$$

There appears to be an error in Semenoff's paper[1] which has been perpetuated in all papers employing his relation. The relation between A and E is given by Semenoff as

$$A = E \frac{\log e}{2R} = E (.11)$$

whence $E = 9.9\ A$

This latter is obviously in error, and should be, as it stands 0.09. The real value of $2R/\log e$ is however nearer 9.2.

The neglect of the variation of $\ln T_o$ with temperature is confined in the above solely to the right hand side of the equation. If simultaneously neglected on the left hand side we would have:

$$\ln p = A/T_o + B$$

an equation which will therefore involve twice whatever error is involved in the first form and which might at first sight therefore also be considered negligible. This unfortunately is not so since as may be shown the neglect of the variation of $\ln T_o$ with temperature is almost balanced by the simultaneous neglect of the higher powers in the binomial expansion of $\sqrt{1 - 4RT_o/E}$ with the result that the $\ln p/T_o$ form is fortuitously more accurate than the $\ln p$ form.

The difficulty of demonstrating this in the general case of equation (8) owing to its complexity may be circumvented by calculations using the actual data available in the hydrogen sulphide oxidation. The value of A using the $\ln p/T$ equation which is given by Thompson as "about 2050" is by actual calculation 2010 whether all of the data quoted by Taylor and Livingston are used or merely those used in the plot by Thompson. The energy of activation according to Semenoff ought thus to be very close to 20,000 calories.

Assuming a value of $E = 20,000$ calories we may by equation (8) calculate the values of $\ln p/T$ at say 500 and 550° K which is within the range studied. A substitution of these values in the equation

$$\log p/T = A/T + B$$

will give for A the correct value it should have to satisfy the observed data by this form of an equation. Calculation shows this value of A to be 1950, that is somewhat less than the observed value 2010.

This deviation is due however to two separate approximations as may be seen by taking merely the next term in the binomial expansion of the root. Taking

$$(1 - 4RT_o/E)^{\frac{1}{2}} = 1 - 2RT_o/E - 2R^2T_o^2/E^2$$

[1] Z. Physik, **48**, 571 (1928).

the general equation (8) becomes:

$$\ln p/T_o = \left(\frac{E}{2RT_o} - \frac{E}{2E + 2RT_o}\right) + \ln E^{\frac{1}{2}}\left(\frac{2RT_o}{E} + \frac{2R^2T_o^2}{E^2}\right) + K$$

Comparison with equation (9) shows that the use of $E/2RT_o$ as equal to $A/T°$ will yield a value for A which is too great, whilst neglect of the variation with temperature of the second term on the right due to its incorporation in B will yield a value that is too low. These errors approximately neutralise each other since if we repeat the above calculation of A, assuming $E = 20,000$ calories, between 500 and 550° K using however (9) instead of (8) a value of 1945 is obtained which may be compared with the 1950 derived from the exact equation. It is furthermore actually possible to evaluate each of these variations separately and confirm the above result.

There appears then no especially good reason to attempt to simplify the general equation (8) even if such were possible since the results of log p/T = A/T + B are fortunately quite good despite the fact that it can theoretically hold only under conditions where no explosion could occur.

There remains only to emphasize one or two points in the paper by Taylor and Livingston in connection with certain criticisms by Thompson. It is apparently tacitly assumed by Thompson that the conditions prevailing in the two sets of experiments are similar. Taylor and Livingston however pointed out that using gases which had been dried over phosphorus pentoxide, the reaction rates were erratic but consistently slower the longer the period of drying and in consequence used throughout the work, gases saturated with water vapor at 21°C. Reproducibility was then quite good provided a thorough cleansing of the system was made before each run. Again, the experiments of Taylor and Livingston were carried out in a spherical bulb of 300 ccs. capacity and approximately 8 cms. in diameter. This would correspond with a ratio of surface to volume of about 0.75 as compared with the smallest ratio used by Thompson and Kelland[1] of 1.3 increasing to 7.8 for another vessel used by them. Accepting the chain nature of the reaction this ratio is of considerably less importance than the fact of the vessel diameter being 8 cms. in comparison with 3.2 in their widest vessels. Such a difference would mean for a chain reaction, less frequent breaking of chains by the walls and a consequently greater proportion of reaction in the gas phase. The fact that the minimum explosion pressures observed by Thompson and Kelland are considerably higher at a given temperature than those found by Taylor and Livingston confirms this point. Hence with moist gases as opposed to extremely dry ones (Thompson and Kelland fractionated the hydrogen sulphide having frozen it in liquid air) and with a wider reaction system, it would appear a gratuitous assumption to postulate that the proportion of heterogeneity in the reaction was the same in the two cases merely because the temperature was the same. The energy of activation measured need not then correspond to that of a surface reaction particularly since in addition to the

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[1] J. Chem. Soc., **1931**, 1809.

above, the data used were obtained at temperatures and pressures only just below the explosion limit. At the same time an attachment of any special importance to the value 18,000 calories obtained by Thompson and Kelland is uncalled for owing to the "extensive averaging," actually over a range from about 9,000 to 40,000 calories in individual experiments.

In conclusion the statement by Thompson that "the experimental evidence on the effect of ultraviolet light upon the system at room temperatures offered by Taylor and Livingston would apparently speak against such a mechanism (a primary dissociation of hydrogen sulphide) since no oxidation occurred despite dissociation of the hydrogen sulphide" would not appear to be a logical conclusion in view of the fact (as pointed out by Taylor and Livingston) that the photochemical oxidation of hydrogen is very difficult since oxygen does not commence to absorb appreciably above 1950 Å whilst hydrogen only below about 1030 Å.

Nichols Chemical Laboratory,
New York University, New York, N. Y.

A CATALYST CHAMBER

BY SAMUEL YUSTER

Research on catalytic reactions often requires numerous changes of catalysts. This becomes rather bothersome in all glass apparatus in which the catalyst chamber is sealed into the line. In order to eliminate this trouble, the chamber described in this article was designed and found to work very satisfactorily.

It has the advantages of being quickly removed, allowing for a quick change of catalyst, and requiring no glass wool to hold the catalyst in place.

The chamber A is joined to the rest of the apparatus by a ground-glass joint which is lubricated with ortho phosphoric acid. A tubular electric furnace is used to heat the chamber.

The gas enters the apparatus at X and goes down through B, which preheats the gases and brings them to the catalyst temperature before they are in contact with it. The gases react while passing through D and the products of the reaction plus any unused gas pass out through Y. C is an annular well which holds the thermometer or thermocouple that indicates the catalyst temperature. A is held to the rest of the apparatus by means of wire or small springs and the arms E, F, and G.

FIG. I
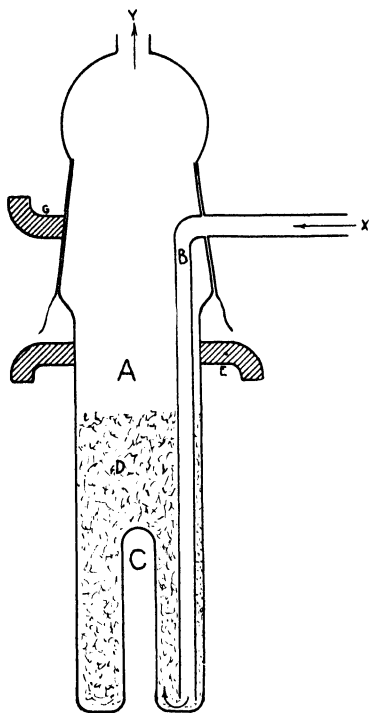
No glass wool is required to hold the catalyst in place if the apparatus is used in the position shown. The elimination of the use of glass wool might mean the removal of a complicating factor in some reactions due to the catalytic effect of the large surface exposed.

The tube may be made as long as is convenient; in fact, it is recommended that the ground-glass joint be far enough away from the furnace to prevent excessive heating.

The writer wishes to acknowledge the help received from Dr. L. H. Reyerson during the design and construction of this piece of apparatus.

TITRATION CURVES FOR ALUMINUM SALTS WITH ALKALIES

BY HERBERT L. DAVIS AND ESTHER C. FARNHAM

During some work now in progress on the preparation of color lakes with alumina it was observed that the sodium salt of an acid dye is capable of doing the work of far more than an equivalent amount of alkali in precipitating alumina from solutions of aluminum salts. In similar fashion, far less alkali is needed to produce the first permanent turbidity of alumina from solutions of aluminum sulphate than from solutions of aluminum chloride, and the alkali needed in both cases increases with dilution of the salt. The explanation in these cases is that the sulphate ions and the dye anions are adsorbed very strongly and cause the neutralization of the positively charged colloidal alumina much more easily than does the less strongly adsorbed chloride ion.

These observations raised questions concerning the titration of such aluminum salts and alkalies as have been given as proof of the formation of such salts as $NaAlO_2$ in the alkaline solutions. The present paper reports a repetition of these titrations under varying conditions of concentration, and it is shown that in these titration curves there are no inflection points corresponding to the amount of alkali needed to begin the precipitation of alumina while in the more concentrated solutions and especially in the sulphate solutions there are inflection points which correspond roughly to the disappearance of the visible particles of alumina at pH 10.5-11. These points are achieved in every case with less than four mols of alkali per atomic weight of aluminum and are affected by dilution and by the nature of the anion present. They do not, therefore, prove the compound formation but are strong evidence for the peptization of alumina by hydroxyl ions.

The earliest work on this subject is contained in the classical paper by Joel Hildebrand[1] on "The Hydrogen Electrode in Analysis, Research, and Teaching." In this paper Hildebrand included the curve for the titration of aluminum sulphate (history, purity and concentration are not stated) with sodium hydroxide. The curve thus obtained is closely similar to that soon after published by Blum[2] for the titration of aluminum chloride. "The aluminum chloride solution, prepared from the recrystallized salt, was about decimolar (for $AlCl_3$) and contained some free hydrochloric acid: the sodium and potassium hydroxide solutions prepared from the metals were about fifth-normal. The initial volume of the titration was about 50 cc." Blum knew of the work of Hildebrand and says: "Subsequent to the appearance of

[1] Hildebrand: J. Am. Chem. Soc., 35, 863 (1913).

[2] Blum: J. Am. Chem. Soc., 35, 1499 (1913).

the paper by Hildebrand, the experiment shown in curve B (AlCl₃ + NaOH) was repeated and continued until considerable excess of alkali was present. No evidence was found, however, of another point of inflection corresponding with the second hydrogen of aluminic acid, the possibility of which was noted by Hildebrand."

Blum's Curves
A– HCl + NaOH
B– AlCl₃ + NaOH
C– AlCl₃ + KOH
Hildebrand's Curve
D– Al₂(SO₄)₃+ NaOH
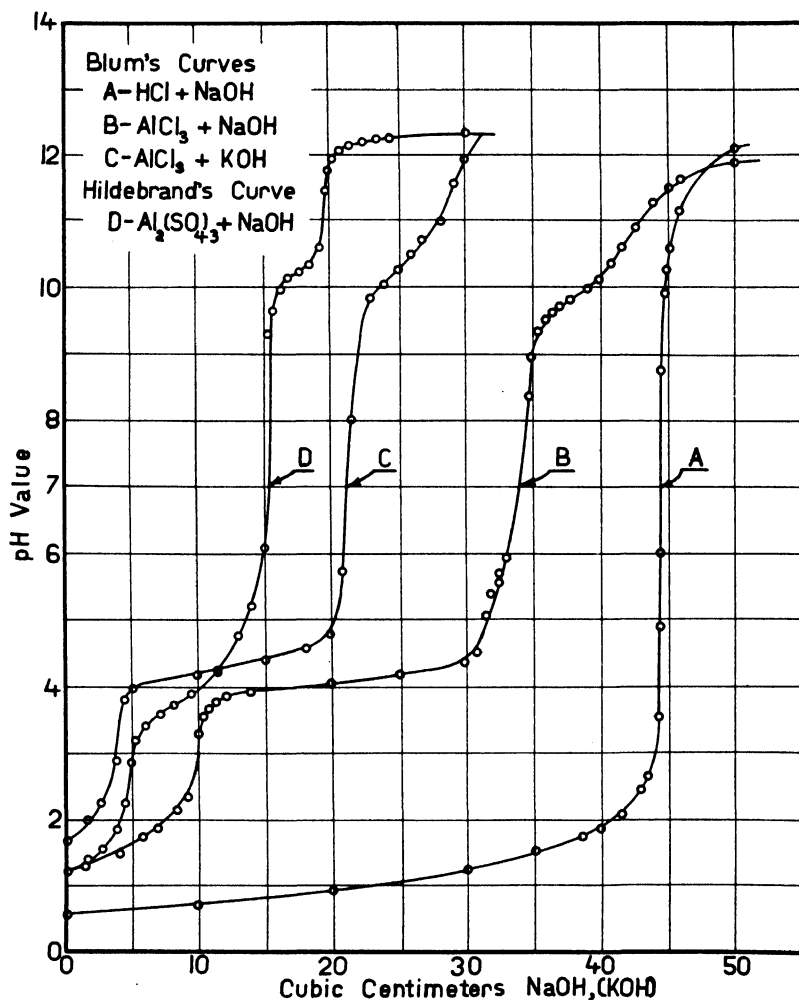
FIG. 1

The titration curves of these two aluminum salts, sulphate and chloride, are found to be closely similar, each possessing the same three break-points in the curve of pH against alkali added. Both authors took as quite significant the points at which the slope of the curve changes, these being analogous to the inflection points which mark the end of titration acid by a base. These curves are shown in Fig. 1 and the pH values of the inflection points are shown in

Table I together with the alkali required to bring the solutions to those pH values. Only the ratios of the volumes used are significant since the concentrations are uncertain.

<div align="center">TABLE I</div>

<div align="center">Break Points in Titration of Aluminum Salts</div>

pH of solutions at break points	1.5	3	7	10.5	11
Alkali used (Hildebrand $Al_2(SO_4)_3$)	0	5 cc	14	—	18
Alkali used (Blum $AlCl_3$)	0	9.8	34	42	—

For the interpretation of these curves we turn first to Blum who was more explicit. "The curve A for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of metals precipitable by hydroxides. It also furnishes a means for determining the points of inflection in the precipitation curves, i.e., the points of departure from a normal neutralization curve. From the curve B for the action of sodium hydroxide upon aluminum chloride, it may be noted that precipitation of aluminum hydroxide begins when (H$\cdot$) is about 10^{-3}, and is complete before (H$\cdot$) is 10^{-7}. The abscissa between these two points, i.e., from 9.8 to 34 cc, or 24.2 cc, represents the volume of sodium hydroxide required to precipitate the aluminum present. The portion of the curve from (H$\cdot$) = 10^{-7} to (H$\cdot$) = $10^{-10.5}$ represents the dissolving of aluminum hydroxide in sodium hydroxide, the solution being almost entirely clear at the latter point. That the solution then contains a definite compound consisting of one atom of sodium to one of aluminum is indicated by the fact that the volume of alkali from the neutral point to this point of inflection, or from 34 to 42 cc is 8.0 cc., i.e., almost exactly one third of the volume (24.2 cc.) required to precipitate all the aluminum. This confirms the observation of Prescott[1] hat one molecule of freshly precipitated aluminum hydroxide dissolves in exactly one molecule of sodium or potassium hydroxide. The same relation holds true in curve C for aluminum chloride and potassium hydroxide where the volumes of alkali required to precipitate and to redissolve the aluminum hydroxide are respectively 17.5 cc. and 6.5. cc. The determination of the exact point of inflection when the aluminum hydroxide is all dissolved is rendered difficult by the partial conversion of the colloidal form as first precipitated, to the crystalline variety, which is difficulty soluble even in great excess of alkali. On standing for several hours some crystalline aluminum hydroxide always separated from the alkaline solutions. The difficult solubility of the last traces of aluminum hydroxide, even with considerable excess of alkali, was more marked with potassium than with sodium hydroxide. No reason is advanced for this difference. Its effect upon the curve for potassium hydroxide and aluminum chloride was practically eliminated by first determining the precipitation portion of the curve, i.e., to 20 cc. of potassium hydroxide, and then starting with a fresh portion of solution, making a single addition of 20 cc. potassium hydroxide and completing the curve in 1 cc intervals. By

[1] Prescott: J. Am. Chem. Soc., **2**, 27 (1890).

this means the time in which the aluminum hydroxide could change to the crystalline difficulty soluble variety was reduced to such an extent that an almost perfectly clear solution was obtained at the point of inflection, *i.e.*, $(H) = 10^{-11}$."

Hildebrand is more nearly correct in the interpretation of his sulphate curve and his observation of the precipitation for he says: "Aluminum hydroxide is precipitated while the solution of aluminum sulphate is still strongly acid, the hydrogen ion concentration during the precipitation varying roughly between 10^{-3} and 10^{-5}." He does, however, see in his curve the formation of aluminate. "The solution of aluminum hydroxide in an excess of alkali is indicated by the final portions of the curve. It will be seen that the proportion of alkali used corresponds to the formula of $NaAlO_2.nH_2O$. There seems also to be a slight break in the curve corresponding to the addition of another equivalent of base. This cannot be regarded as certain until confirmed by more accurate measurements. We believe, however, that the curve here given supports the theory of the solution of aluminum hydroxide as an acid rather than as a colloid, as claimed by Mahin, Ingraham, and Stewart.[1] The ultramicroscope, which these investigators seem not to have applied and which should give rather decisive evidence for or against a colloid theory fails to show the presence of a colloid in this solution, although the ordinary solutions of aluminum hydroxide produced by dialysis show submicrons very plainly in the ultramicroscope."

Blum also asserts that his titration shows the existence of $NaAlO_2$ and $KAlO_2$ and continues: "If this process of solution were due entirely, or even principally, to the colloid properties of aluminum hydroxide there would probably be a reduction in the alkalinity of the solution, but it is improbable that it would be of such magnitude as has been shown here, much less that the maximum reduction in alkalinity would occur when the alkali was chemically equivalent to the aluminum hydroxide." The present paper demonstrates that this statement is generally not in accord with the facts.

These titrations of Hildebrand and of Blum have been accepted by Weiser[2] as the best available evidence to prove the existence of aluminates in alkaline solutions as against the colloidal peptization of alumina by alkalies. It appears wise to review the whole problem in the light of some similar experiments done more recently which are more in accord with what we might expect of such systems. In the first place the essential identity of these curves is their undoing and shows either that one or both of these curves are in error or that such titrations show no unique points related to the precipitation of alumina. The close similarity of the titration curves for these salts is confirmed by our own experiments but it becomes evident that this is because they represent a common reaction, the neutralization of the acid freed by hydrolysis of the salts. This is the view later expressed by Blum[3] in discussing the estimation

[1] Mahin, Ingraham, and Stewart: J. Am. Chem. Soc., 35, 30 (1913).
[2] Weiser: "The Hydrous Oxides," 117 (1926).
[3] Blum: Bur. Standards Sci. Paper, 286 (1917).

of aluminum. He said that the precipitation of alumina "may be considered as a progressive hydrolysis brought about by the neutralization of the acid continuously set free."

The later investigations of Miller[1] will throw some light on this question although, unfortunately, he employed very dilute solutions so that his conclusions might be applied to water purification. Thus the titration of 0.005 molar potassium alum solution and of 0.01 molar aluminum chloride solution gives two curves which are very similar. With the first addition of alkali there is a slow increase in pH and then with the addition of the last half of an equivalent of sodium hydroxide the pH of the solutions increases sharply from 5 to 9. There is no sign of any inflection of the curve with low additions of alkali such as at pH 3 which could be interpreted as the beginning of the precipitation of alumina, nor is there any sign of an inflection point up to the four mols of alkali added to the atom of aluminum.

Especially interesting are the experiments of Miller that concern the precipitation of alumina directly. Portions of 500 cc of the aluminum salt solutions were precipitated by the slow addition of 500 cc of sodium hydroxide solution with mechanical stirring. The final concentration was 0.005 molar with respect to aluminum. After the addition of the reagent had been completed, the solution was permitted to stand a half hour. The hydrogen ion concentration was determined colorimetrically and the precipitated alumina determined. This experiment gave the data shown in Table II.

TABLE II

Anion Effect on the Precipitation of Alumina

	First Precipitate		Complete Precipitation	
Potassium alum	pH 4.1	required 1.2 NaOH/Al	pH 5.2 − 2.4 NaOH/Al	
Aluminum chloride	7.1	2.9	7.8 − 2.95	

These data are in part extrapolated from the curves and data of the paper but they are essentially correct. The smallest actual amount of alkali added to the sulphate solution was 1.2 mols NaOH per atom of aluminum and this gave a precipitate of 32% of all the alumina at pH 4.3, while when 2.4 mols of alkali were added, 98% of the aluminum precipitated at pH 5.2, and 2.7 mols of alkali gave complete precipitation at pH 6.7. In the case of aluminum chloride the addition of 2.9 NaOH gave no precipitate even though the pH was 7.1 while the use of 2.95 mols of alkali brought down 99% of the available alumina at pH 7.8. A further study of these data reveals that the range for complete precipitation of the alumina from chloride solution is a narrow one included within the limits of pH 7.8 to 8.5, while from sulphate solutions practically complete precipitation is achieved over the wide range from pH 5.2 to 8.0. This work of Miller taken in connection with the earlier work of Theriault and Clark[2] demonstrates that the width of these precipitation areas as

[1] Miller: U. S. Public Health Reports, 40, 351 (1925).
[2] Theriault and Clark: U. S. Public Health Reports, 38, 181 (1923).

well as their actual position depends on the concentration of the salts and upon the anions present. By the addition of ammonium chloride, Miller found the precipitation area for chloride alumina to be extended from 6.2 to 9.5 and a titration of aluminum chloride with potassium carbonate gave a curve very like that obtained from the sulphate and alkali except that the carbonate curve is displaced about one unit to a higher pH value.

One other set of experiments by Miller is interesting. He found it possible to coagulate the aluminum chloride mixtures containing deficient amounts of alkali if he added sodium sulphate. His table is reproduced as Table III. "In Table III are given data showing the smallest quantities of sodium sulphate which, when added to one liter quantities of 0.005 molar aluminum chloride-sodium hydroxide mixtures cause complete flocculation of the colloidal material, leaving the supernatant liquid clear and sparkling after the floc has settled."

TABLE III

Flocculation of Aluminum Chloride—NaOH Mixtures by Na_2SO_4

pH	4.6	4.9	6.8	8.4	9.0
Mols NaOH/Al	2.0	2.40	2.75	2.90	3.1
Equivalents of Na_2SO_4 per mol $AlCl_3$ 0.7	0.7	0.3	0.2	0.0

These data show clearly the rôle of the strongly adsorbed sulphate anion in effecting the precipitation of the alumina at a much lower pH and with considerably less alkali than would be required in the presence of the chloride ion only. A strongly adsorbed dye anion would have a comparable effect.

As a first approximation, then, we have that the addition of 3 NaOH per atom of aluminum to a chloride or sulphate solution will result in the complete precipitation of the alumina and will give a solution of about pH 8 to 9. Kolthoff[1] found quite empirically that he could titrate aluminum salts with alkali with phenolphthalein as indicator. "Finally I have investigated whether aluminum salts may be titrated with alkali using phenolphthalein as indicator.

"Ten cc 0.1 molar alum neutralized $\pm$ 25 cc 0.1 N NaOH (calculated 30 cc) (Kolthoff is using $KAl(SO_4)_2$ as alum and his solution is 0.3N with respect to aluminum). The end-point was vague. In the presence of an excess of barium nitrate 29.1, 29.2, 29.2 cc 0.1 N alkali was used. When the titration in presence in an excess of barium nitrate was carried out at the boiling point, 30.4, 30.3, 30.3, 30.4 cc 0.1 N alkali was neutralized.

"On cooling, the solution became red again and it required 0.3-0.4 cc 0.1 N HCl to decolorize the phenolphthalein. This method leads to excellent results. The mixture of the alum solution and excess barium nitrate is titrated at the boiling point until the color of phenolphthalein is pale pink. The solution is cooled and the small excess of alkali is titrated with acid.

"The experiment was repeated with aluminum chloride solution which was 0.151 N (standardized by silver nitrate according to Mohr, with an excess of

[1] Kolthoff: Z. anorg. Chem., 112, 172 (1920).

magnesium oxide). Ten cc at room temperature required 14.75, 14.70 cc 0.1 N alkali with phenolphthalein (calculated 15.1 cc). At the boiling point 10 cc required 15.20, 15.22 cc 0.1 N alkali; after cooling it was back-titrated with 0.12, 0.15 cc 0.1 N HCl. The results show that the method described is a good one."

Our first attempt to duplicate these results of Kolthoff showed that he had not emphasized sufficiently the necessity of considerable boiling of the sulphate systems. Thus, following his directions, 10 cc of 0.3 N alum (with respect to aluminum) required 29.1 cc 0.1 N alkali and it was only when the solution was heated for about five minutes before addition of alkali and boiled for five minutes after the faint pink of phenolphthalein has been obtained that 29.9 and 30.3 cc were required. It is obvious that the method is not immediately useful for the determination of the amount of aluminum present unless there is some assurance that the aluminum salt used is a neutral salt. Excess acid will be accounted as aluminum and a basic salt will give low values for the aluminum present.

It seemed desirable to have a clearer idea of the reason for this titration and the effect of the variables upon it. Ten cc portions of aluminum chloride and of aluminum sulphate solutions were titrated with 1.19 N NaOH and back-titrated with 0.136 N H_2SO_4. The apparent concentrations of these solutions are shown in Table IV found by titration under various conditions.

TABLE IV

Apparent Normality of Aluminum Salt Solutions

	$AlCl_3$	$Al_2(SO_4)_3$
Cold, no salt	0.975 N	0.940 N
Same after boiling and cooling	0.997	1.003
Cold + 25 cc 0.5 N $Ba(NO_3)_2$	0.988	0.994
Same, boiled and cooled	1.008	1.023
Cold + 12.5 cc N Na_2SO_4	0.940	0.940
Same, boiled and cooled	0.997	1.005

Some very interesting observations of these data can be made. In the first place, with both solutions the blank and the system with sodium sulphate give results which are identical while the addition of barium nitrate requires the use of more alkali. It was shown that in the case of the chloride solution the value obtained by titrating with silver nitrate gave 1.001 N for the $AlCl_3$ confirming the lower titration value and showing that the barium salt titration is in error. Kolthoff was not clear as to whether barium nitrate should be used in the chloride titration but it follows from this that it should not. A glance at the table will show exactly the same relations in the sulphate solutions except the error introduced by the barium nitrate is even larger. If he had tried it, Kolthoff would have found that the sulphate solution too could be titrated without salt addition. The essential difference is that the solutions containing sulphate require much longer heating and Kolthoff merely made the plus

error of barium nitrate addition balance the minus error of insufficient heating so as to arrive at the proper result.

We are now prepared to arrive at an understanding of this titration. The important process is the liberation of the acid produced by hydrolysis and then the separation of this acid from the strongly adsorbing hydrous alumina. Even the original solutions contain colloidal alumina and heating and alkali addition increase the amount of this form until it exceeds the specific solubility under the circumstances, the most important factor being the anions present. This colloidal alumina as formed adsorbs aluminum ions and hydrogen ions and in the presence of sulphate ions these too are adsorbed and tend to neutralize the charge on the alumina and precipitate it. It is clear, then, that the alumina will carry down acid and thus prevent its neutralization until a high pH is reached. The table shows this effect to be greater in the presence of sulphate ions than of chloride ions. Thus the first persistent (not permanent) pink of phenolphthalein makes the chloride solution cold appear to be 0.975 N while the sulphate solution which finally requires the same amount of alkali shows this pink as of 0.94 N, the explanation being that the sulphate is markedly more effective in increasing hydrogen ion adsorption on the alumina. The addition of sodium sulphate to the aluminum chloride has the same effect. Although the sodium sulphate is barely acid to phenolphthalein, its addition to the aluminum chloride makes necessary the addition of 0.3 cc N alkali less in order to obtain the pink color. This is undoubtedly the explanation of the recent work by Thomas and Whitehead.[1] They reported that sulphates when added to solutions of aluminum chloride or sulphate were more effective in raising the pH than chlorides are. Sulphates are more effective in increasing the adsorption of hydrogen ions on alumina and thus raising the pH of the solution so that in the present case it requires less alkali to titrate and therefore appears less concentrated than it really is.

Since the sulphate ion is notorious for its effect on alumina it was logical for Kolthoff to add barium salts to remove that effect. The difficulty is that an excess overcorrects the error and actually no salt is needed if the boiling be sufficiently vigorous and for a long enough time. Thus even excess sulphate added has little effect on the titration under these conditions. But the excess of barium salt appears to act by being adsorbed and in the alkaline solutions increasing the adsorption of hydroxyl ions leading to high alkali requirements. Other strongly adsorbed cations should behave similarly and the addition of 25 cc N $Ca(NO_3)_2$ to an aluminum sulphate titration gave 1.021 N while an equivalent amount of sodium nitrate gave 1.003 N as the concentration of the aluminum sulphate solution. A similar behaviour was shown for barium sulphate when 10 cc N sodium sulphate and 25 cc 0.5 N barium nitrate were made very faint pink to phenolphthalein and then mixed. On boiling the excess barium ion was adsorbed on the barium sulphate and carried down increasing amounts of hydroxyl ion until 0.5 cc 0.1 N alkali had been added to keep the color at the faint pink of the indicator. On cooling one drop of 0.136

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[1] Thomas and Whitehead: J. Am. Leather Chem. Assoc., **25**, 127 (1930); Chem. Abs. **24**, 2659 (1930).

N H_2SO_4 decolorized the suspension so that this experiment shows that adsorption by barium sulphate accounted for about one fourth of the error observed in the titration of the aluminum sulphate in the presence of excess barium sulphate. The high adsorptive power of the alumina accounts for the remainder as it is due likewise to the adsorption of barium and hydroxyl ions. As the table shows, barium ions are effective in reducing hydrogen ion adsorption and in thus freeing a larger amount of the acid for titration cold but on heating in the alkaline solutions they do increase the error. Similarly sulphate ions on the acid side increase acid adsorption but in the alkaline solutions oppose adsorption of hydroxyl ions. Since the titration is to be finished on the alkaline side, the use of sodium sulphate might be indicated. But the table shows that no salt is needed and that salts of the type of barium nitrate are distinctly not to be used.

The conclusions of this matter, then, is that the addition of alkali to cold solutions of aluminum salts will give a pink color of phenolphthalein before three equivalents of alkali have been added and that this error is greater in the sulphate solution than in the chloride solution. This is the definite proof that Hildebrand and Blum by adding alkali to such solutions did not titrate the salt solutions as they believed, but that a pH of 7 was reached with considerably less than the equivalent amount of alkali. In the curves to be shown later the magnitude of this error will be demonstrated and its variation with concentration and anions present. An investigation of 0.1 N $AlCl_3$ and 0.1 N $Al_2(SO_4)_3$ showed that comparable effects are found also in more dilute solutions.

The Explanation of the Curves of Blum and of Hildebrand

We are now prepared to study these curves of Hildebrand and of Blum in more detail and to point out that not only do they include free acid but that they cannot mean the things that their observers interpreted them to mean. The first portion of their curves from pH 1.5 to pH 3 is as Blum intimated due to the presence of excess acid, since this curve is quite like the final portion of the curve of free acid. Further neither Clark nor Miller had any such curve for the salts in question and they were using more refined methods. One comment[1] on the earlier work is of interest. "If these curves are compared with those published by Hildebrand (1913) and by Blum (1913-14), there will be found a general agreement in main features. However the measurements by Hildebrand and by Blum were made with comparatively crude instruments, and for this reason the observers probably hesitated to call attention to the detailed features in the titration curve which must have appeared to them very peculiar. One notable feature is the distinct slope of the curve between pH 5 and 8. The fact that the steeper part of the curve should occur so distinctly ahead of three equivalents of alkali is also food for thought. The flatness of the curve at the start is, of course, accounted for by the throwing out of one or more constituents of the equilibrium as the titration proceeds."

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[1] Theriault and Clark: U. S. Public Health Reports, **38**, 181 (1923).

Our own titrations on salts which were known to be free from excess acid or base shows no first portion of curve from 1.5 to 3 but start from pH values between 2.3 and 3.4 and are very slow to change their pH on addition of alkali. It is probable, but not proved, that excess acid if present would be titrated sharply to pH 3 as these early authors believe.

The next point that should be made is that the essential identity between the curves for the sulphate and chloride titrations is the best evidence that neither tells anything about the start of the precipitation of alumina. The experiments of Clark and of Miller show that alumina begins to be coagulated into particles caught by the filter under quite different conditions of alkali addition and pH. If the alkali be added to 0.1 N aluminum salt solutions and they be heated a little to accelerate equilibrium, it is found that from 80 to 90% of the theoretical alkali may be added to the chloride without producing a permanent precipitate of alumina while to the sulphate solution not more than about 20% can be added. These are systems in equilibrium while the observations in titrations are distinctly not in equilibrium. If the titrations are carried out slowly enough the alumina precipitated by local alkali concentrations on first additions will be dispersed and the chloride solution will stay clear much longer than the sulphate solution. Alkali addition must increase greatly the proportion of aluminum present as alumina before it appears as visible aggregates and this last step will be aided greatly by sulphate adsorption. It is clear therefore that at pH 3 Hildebrand had a rough index of the beginning of titration of the aluminum salts after the neutralization of the free acid and that the formation of visible permanent precipitates of alumina would lag behind this point and will occur for the sulphate before it does for the chloride.

The practical identity of the curves can be related only to the fact that the essential reaction taking place is the titration of the hydrochloric and sulphuric acids set free by hydrolysis. The lag in this hydrolysis causes the pH during the addition of alkali to rise more slowly than if all the acid were free originally. This slow setting-free by hydrolysis makes the strong acids titrate as though they were weak acids merely because of the relatively low free acid concentration in equilibrium with the hydrolyzing solution. The formation of the alumina is then given by the equation:

$$2AlCl_3 + 3HOH \rightleftarrows Al_2O_3.xH_2O + 6HCl.$$
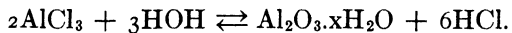
and the displacement of this equilibrium to the right by the neutralization of the acid results in the accumulation of the alumina, first as colloidal positively charged alumina. As its concentration increases, the alumina begins to precipitate but a very important factor is the presence of strongly adsorbed anions capable of neutralizing the original positive charge of the alumina below its critical value and thus bring about the precipitation. In this picture the hydrogen plays only a secondary rôle and it is quite impossible to speak intelligently of the isoelectric point of alumina unless one specifies the other constituents of the system. The center of Miller's precipitation ranges is of the nature of an isoelectric point for alumina but he found this point to be

greatly affected by the anions present. A strongly adsorbed anion will neutralize the positive charge impressed on alumina by a solution of low pH or high hydrogen ion concentration and this low pH will be the isoelectric point for that anion and for that concentration. Similarly alumina precipitated in the presence of the weakly adsorbed monovalent chloride ion will adsorb so little of this anion that the hydrogen adsorbed from a solution at pH 7 or 8 is sufficient to give an aggregate whose charge is below the critical value, and 7 or 8 is the isoelectric point then.

It is, therefore, highly improbable that aluminum chloride should start to precipitate at pH 3 and complete its precipitation at pH 7; and the volume of alkali used between these points can have no such meaning as Blum ascribes. The use of one third of this amount to redisperse the alumina is sheer coincidence and it did not favor Blum when he used potassium hydroxide, the titration being at least 10% in error. The explanation of this is that the excess alkali is dispersing the alumina as a colloid and the difference between sodium and potassium hydroxides is to be ascribed to a different adsorption for the potassium and sodium ions. It has already been shown that it is quite impossible for aluminum sulphate to give a curve identical with that of the chloride if the break points were unique for the alumina produced.

We may conclude then that this first break point at pH 3 is an approximate measure of the free acid present. Aluminum chloride and sulphate are notorious for forming acid of basic salts but potassium alum is crystallized in better form and Miller with this salt observed no free acid. Our runs on neutral salts show none. This point on the early curves drops out of consideration.

The second point of interest is at pH 7 which they selected as the equivalent point. Our experiments show that this is below the amount of alkali required for real titration and that it varies with the anion. Further, the curve as it passes through pH 7 has a distinct slope and is not vertical as it is for free mineral acid.

By far the most interesting points on these curves are the break-points at pH 10.5 to 11. It has been shown that the relative volumes of alkali required for these points was nearly one third more than that required to reach pH 7 with sodium hydroxide. It must now be emphasized that neither Hildebrand nor Blum showed that these were in the ratio of 3 NaOH/Al and 4NaOH/Al. Our own experiments agree with this as to the relative amounts of alkali used; but the actual figures come out about 2.6 NaOH and 3.7 NaOH for the sulphate and about 2.7 NaOH and 3.4 NaOH for the chloride titration. There is in these figures no support for any conclusion as to the sharp formation of sodium aluminate.

The Titration Runs

In order to study these curves in more detail, solutions were prepared to be N, 0.3 N and 0.1 N with respect to aluminum chloride and aluminum sulphate and sodium hydroxide. The salts used were of the best grade and had been previously studied by the precipitation of alumina and sulphate and by the silver nitrate titration. They were thus established as neutral

aluminum salts without free acid or base, and the solutions prepared were standardized by comparing them with the alkali solution according to the method of Kolthoff. In each case thirty cc portions of the aluminum salt

Titration Curves
AlCl$_3$ + NaOH
o N Solutions
• .3N Solutions
o .IN Solutions
⬥Electrode left
in (.3N Sol)
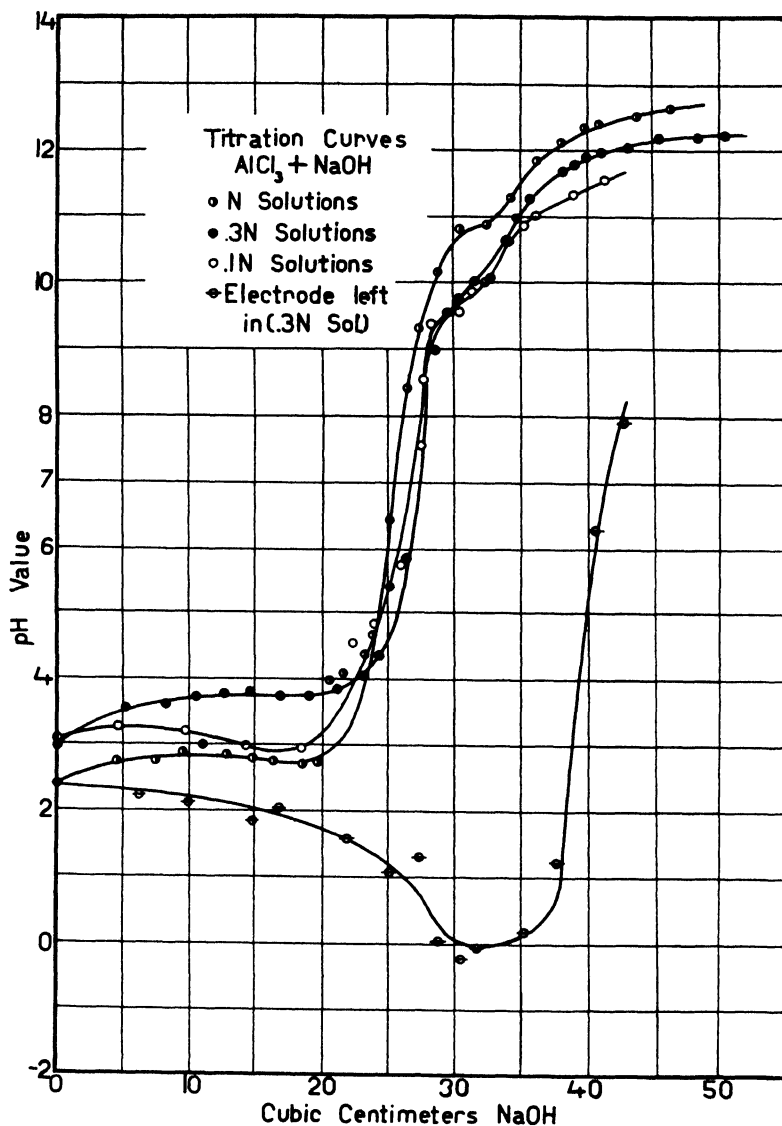
Fig. 2

solutions were titrated in an open beaker stirred by hydrogen bubbling over a strip of platinized platinum electrode. Hydrogen from a commercial cylinder was purified by passage through alkaline pyrogallol, sulphuric acid and water. The alkali of the same concentration as the salt solution was added in 1–2 cc portions. This procedure provides a constant volume in

each titration although the concentration changes, and in each case 30 cc of alkali is equivalent to 3 NaOH/Al. The saturated calomel half-cell was used with a potassium chloride bridge, the value for this being taken as

Titration Curves
$Al(SO_4)_3$ + NaOH
○ N Solutions
● .3N Solutions
○ .1N Solutions
↝ Electrode left
  in (.3N Sol.)

HCl + NaOH

pH Value

Cubic Centimeters NaOH
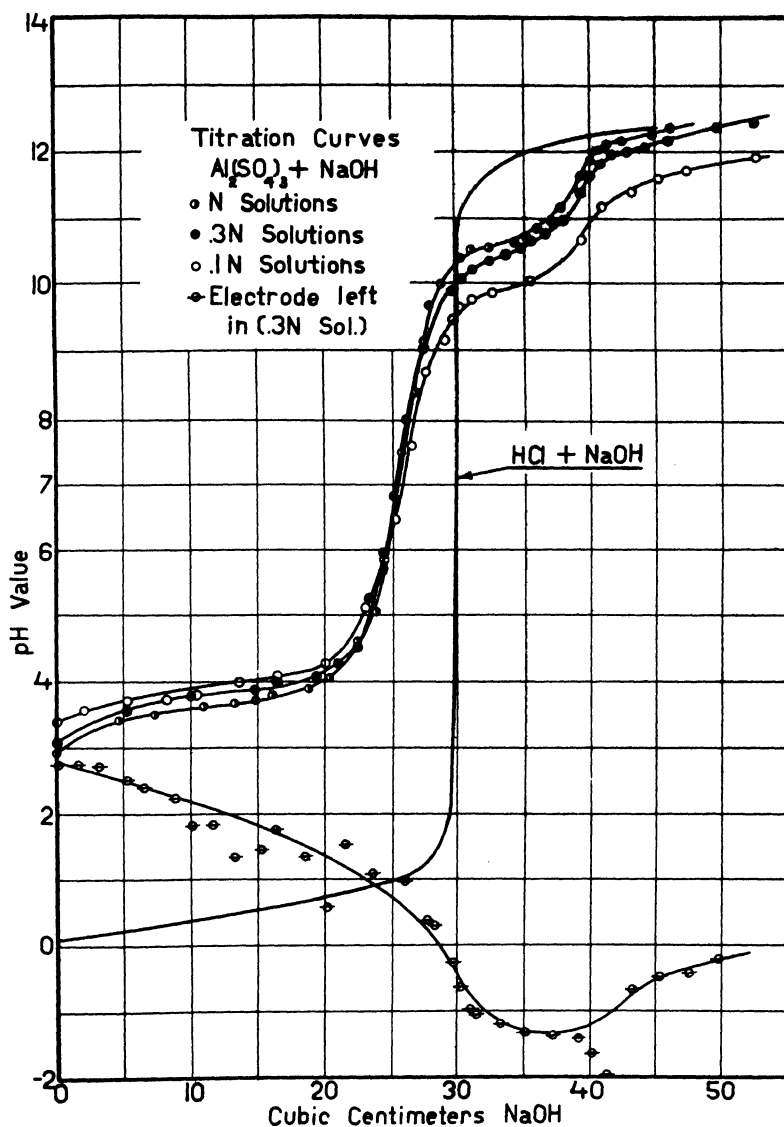
FIG. 3

0.245 volts at 25°. All determinations were made at room temperature and corrections made for 25°–30°.

Although neither Blum nor Hildebrand mentions removing the electrode during the alkali addition, it appears that both must have done so. Permitting the electrode to remain in the solution during the addition of the

alkali causes the deposition of a thick coating of adherent alumina on the electrode and this gives very unsatisfactory results. Typical curves for such titrations are shown in Figs. 2 and 3 for 0.3 N AlCl$_3$ and 0.3 N Al$_2$(SO$_4$)$_3$, approximately the concentration used by Hildebrand and Blum. In these curves it is observed that on adding alkali to the aluminum salt solutions, the apparent hydrogen ion concentration of the solution actually increases. This may bring about a reversal of the cell and the calculations show that in the case of the sulphate the apparent hydrogen ion concentration of the solution is of the order of 100 N, a perfectly fantastic figure.

This represents striking poisoning of the electrode by the alumina which is coagulated upon it. Originally this alumina is highly adsorptive and as formed carries on to the electrode with it adsorbed hydrogen ions in the hydrous sheath. This however would not account for a continued increase in the apparent hydrogen ion concentration of this adsorbed layer and furthermore it is, in the present state of our knowledge, questionable whether adsorbed hydrogen ions are capable of affecting a hydrogen electrode. For the present no full explanation can be given of this phenomenon and it appears to be comparable to the ordinary poisoning processes already known about. This may have in this case a mechanical action by which the continuously increasing film of alumina prevents the access of the hydrogen gas to the electrode and therefore the setting up of the equilibrium between molecular and atomic hydrogen upon which the action of the electrode depends. It may be merely that the alumina blocks off this activating adsorption of the hydrogen on the platinum. Whatever the mechanism may be it is clear that the observed poisoning effect will be calculated as an apparent high hydrogen ion concentration in such systems. Actually of course the free solution is much more alkaline than the electrode shows, for phenolphthalein changes color when about 80-90% of the theoretical alkali has been added although the apparent pH by the electrode is still far on the acid side of pH 7. The continued addition of alkali has a peptizing action on the alumina layer so that in the case of the chloride a pH value of 7 is shown by a little more than 4 NaOH/Al although phenolphthalein turns pink at about 2.7 NaOH/Al. In the case of the sulphate solution the peptization of this layer appears more difficult and even 5 NaOH fails to produce a solution which is alkaline according to the electrode.

In view of these gross abnormalities the procedure was adopted of withdrawing the electrode from the solution during the addition of the alkali although stirring was continued by means of the hydrogen. Two to five minutes were allowed for the precipitation of the alumina, the electrode was replaced and the equilibrium reading obtained. This method is a great improvement over the first one and is apparently the one used by Hildebrand and by Blum since it gives curves similar to theirs. It is, however, not a full solution to the problem for even thus a film of solution adhering to the electrode contains some alumina which tends to form a light film on the electrode when the latter is reimmersed in the solution which has in the meantime become more alkaline. This light film should have some such

effect as the heavier one has been shown to have so that the curves given may be at a somewhat lower pH than the solution itself. That this error is a very slight one is shown by the fact that the readings of the electrode agree in most of the cases with the first appearance of the pink color of phenolphthalein which was added to all titrations. It is quite probable that the deviations increase with departure from neutrality and that a better way to study this system would be by portions made up separately and permitted to come to equilibrium before the electrode is used. The values recorded are approximately correct and are comparable among themselves.

TABLE V

Titration of Aluminum Chloride with Sodium Hydroxide

	N AlCl$_3$		0.3 N AlCl$_3$		0.1 N AlCl$_3$	
	NaOH	pH	NaOH	pH	NaOH	pH
Original solution	0	2.3	0	2.9	0	3.0
Phenolphthalein	25.2	6.4	26.3	5.8	27.0	7.5
showed pink	26.5	8.4	27.4	8.4	27.75	8.5
At 3 NaOH/Al	30	10.7	30	9.7	30	9.3
Break points	34.5	11.0	33	10.1		
At 5 NaOH/Al	50	12.7	50	12.2	50	11.7

TABLE VI

Titration of Aluminum Sulphate with Sodium Hydroxide

	N Al$_2$(SO$_4$)$_3$		0.3 N Al$_2$(SO$_4$)$_3$		0.1 N Al$_2$(SO$_4$)	
	NaOH	pH	NaOH	pH	NaOH	pH
Original solution	0	2.8	0	3.0	0	3.4
Phenolphthalein	26	7.4	25.2	6.8	26.3	7.5
showed pink	27	8.4	26.3	7.9	27.4	8.6
At 3 NaOH/Al	30	10.4	30	10.1	30	9.6
Break points	37.5	11.2	37.5	10.9	37	10.2
At 5 NaOH/Al	50	12.6	50	12.4	50	11.8

In Tables V and VI are shown those data from the two titrations which are significant, including under each concentration of salt the volume of alkali added (of the same normality as the salt) and the pH value observed. The pH of the chloride solutions is lower than that of the corresponding sulphate solutions and in both the acidity increases with concentration. Next are shown the volumes of alkali and the pH readings before and after the phenolphthalein showed its first pink color. In all cases save one these pH values are on opposite sides of pH 8.3 the lower end of the phenolphthalein range. This checks the correctness of the electrode reading at this point and since in no case is more than 27.75 cc of alkali required to pass the pH 8.3 this shows that the Hildebrand and Blum assumptions that all the alumina was titrated at pH 7 is at least ten per cent in error. This is confirmed by the pH values observed when 3 NaOH is actually added in each system,

the lowest pH being 9.3, which is quite different from 7. As break-points are shown those volumes of alkali and the corresponding pH at which the curves appears to change direction in the irregular portion and finally are shown the pH values obtained on addition of 5 NaOH/Al. The tables should be compared with the curves in Figs. 2 and 3 where the complete systems are shown.

The first item of interest is that there is no break in these curves corresponding to those found by Hildebrand and by Blum at pH 3 and which we have explained as being due to the free acid present. Further there is no irregularity in these curves which might be taken as the beginning of precipitation of alumina. This is difficult to observe under the conditions of the experiment but approximately four to five cc of alkali gave precipitates in the sulphate solutions which did not clear while the electrode was coming to equilibrium while in the chloride solutions three times this amount of alkali gave a temporary precipitate which cleared before the next addition of alkali. This is in accord with what would be expected and with the 20 and 80% additions when time for equilibrium was allowed. It is, therefore, somewhat hazardous to state definitely just what amount of alkali gave a visible precipitate of the hydrous alumina; it is clear that there is a marked difference between chloride and sulphate in this repect. At any rate the agglomeration of the alumina to particles large enough to see is probably not a unique point but merely a stage in a continuous process.

The courses of the two sets of curves are quite similar, both being fairly flat between pH 3 and 4 until 2 NaOH has been added when there is a sharp but not a vertical ascent ceasing shortly before 3 NaOH/Al is reached. If any point were to be taken as marking the end of the precipitation of the alumina, it might be at 2 NaOH for there the flat ceases. But common experience in determining alumina precludes the acceptance of this point. The gradual increase in pH with alkali addition on the steep portions of these curves confirms the observations of Clark and distinguishes these curves from a true titration curve. In all these aluminum salt curves the change from pH 4 to pH 10 requires approximately 10 cc of alkali while a similar change in the titration of hydrochloric acid requires only a drop or two. This is, of course, a type of buffer action in which the precipitated alumina, having adsorbed the hydrogen ion gives it up slowly as the solution becomes alkaline. This buffer action is particularly marked in the acid range and if one did not mind the alumina present, aluminum chloride-sodium hydroxide buffers might be made for the range from pH 3 to 4. The adsorption of the acids by alumina makes the systems titrate as relatively weak acids instead of the strong acids HCl and H_2SO_4 actually are.

The curves also show graphically that it is impossible to titrate these systems cold using phenolphthalein or any other indicator since there is no vertical portion of the curves at 3 NaOH/Al. Heating swings the lower end of the steep portion of the curves to the right and makes the curves approximately vertical at the pH 8.3 of phenolphthalein, since heating reduces the acid adsorption. This is all in agreement with the Kolthoff method of titrating these salts.

The most interesting point in connection with these curves is that they show break-points such as were reported by the earlier authors at pH 10 to pH 11, and further that these points do coincide roughly with the apparent final disappearance of visible particles of alumina. There is some reason to believe that this may be an error in observation and this point will be studied further. The data show, however, that these points come at about 34 cc of alkali for the chloride systems and about 37 cc for the sulphate solutions. These break-points differ in pH with the concentration of the salt and with the anion present, although the volumes of alkali needed for the various concentrations are approximately the same for each of the two salts separately. The volumes of alkali used are about 34 cc for the chloride solutions and 37 cc for the sulphate solutions and by no stretch of the imagination could these be taken as 4 NaOH/Al. In these curves too the volumes of alkali needed to bring the systems to pH 7 and then to this second break are roughly in the 3:1 ratio but the actual values are for the chloride system 2.6:0.8 NaOH/Al and for the sulphate 2.6:1.1 NaOH/Al.

The failure of these points to come out in simple stoichiometric proportions removes the last support for the theory of aluminate formation in these alkaline solutions. The explanation then is to be sought in a peptization of the alumina by the hydroxyl ions. The tendency to a flattening of the curve in the alkaline solution shows that the added alkali is disappearing from the solution by being adsorbed on the alumina until the latter is dispersed and saturated with hydroxyl ion. Then further alkali addition builds up a free hydroxyl ion concentration in the solution comparable to that obtained in the presence of sodium chloride only and the curves assume the shape of the HCl curve.

If there were merely adsorption of the alkali on the alumina and one measured the pH of the intermicellar liquid, the pH of the systems containing alumina should be lower than that of the HCl–NaOH titration in the alkaline range. The more alumina present should adsorb more alkali so that the curve for the normal solution should come lowest of all. The observed order is the reverse of this and the normal solution is as strongly alkaline as the system containing no alumina. This is merely another result of the deposition of a film of alumina on the electrode. In the alkaline solution this film by adsorption of hydroxyl ion makes the electrode appear to be in an abnormally alkaline solution and this error is greater in the more concentrated solutions. The thinner layers of alumina are more easily peptized from the electrode. Up to the break-points the hydroxyl ions are peptizing the outer layers of alumina on the electrode and then the sharp upturn denotes the adsorption of these ions on the lower layers until these become saturated. The marked difference in the shapes of these upper irregular portions of the curves is further evidence that we are dealing with peptization and not compound formation. The sulphate alumina is easier to precipitate and harder to peptize than the chloride alumina and this is mirrored in the greater change of direction of the sulphate curve. The gradual disappearance of this irregular portion with dilution is significant and explains why Clark and Miller did not observe it in their very dilute solutions.

Summary

1. The alkali titration curves of Hildebrand for aluminum sulphate and of Blum for aluminum chloride have been considered as the best available evidence for the formation of aluminates in aklaline solutions.

2. These titrations have been repeated and the general features of the curves confirmed except in so far as the earlier work was done on salt which contained free acid.

3. Such titrations have been made also for more dilute and more concentrated solutions and it becomes evident that the interpretations previously offered are not valid. The breaks in the curve are not unique for alumina alone but are influenced by the conditions.

4. There is no break or irregularity in the titration curves corresponding to the beginning of the precipitation of alumina. Some colloidal alumina is present in the original solutions and its quantity and aggregation increases steadily with alkali addition. Visible and filterable particles of alumina appear at markedly different alkali additions which depend on the concentration, the temperature, and the anions present.

5. It is shown that aluminum salts can be titrated with alkali if boiled, and that salt addition is not necessary and is in some cases actually bad practice.

6. It is shown that aluminum salts cannot be titrated cold by adding sufficient alkali to bring the system to pH 7 as was believed by Hildebrand and Blum. The volumes of alkali used for this and for the break in the curves at pH 10 to 11 are not in the simple ratio of 3 and 4 NaOH per atomic weight of aluminum and therefore lose all value as a proof of compound formation in the excess alkali.

7. Since the beginning or the end of the precipitation of alumina produces no inflection points in these curves their similarity of form is to be ascribed to the common reaction occurring, namely the neutralization of the hydrochloric or sulphuric acids as this process is affected by their adsorption on the alumina.

8. It is shown that alumina deposited on the hydrogen electrode can cause very large errors in the readings obtained.

9. This paper shows that the action of alkalies on alumina is one of dispersion and that this process is affected by such factors as concentration and particularly by the difference between sulphate and chloride ions which should affect the adsorption of the peptizing hydroxyl ion.

Cornell University.

NEW BOOKS

The Structure of Crystals. *By Ralph W. G. Wyckoff. Second edition. 23 × 16 cm; pp. 497. New York: Chemical Catalog Company, 1931. Price: $7.50.* This is one of the Chemical Society Monographs. The first edition was reviewed seven years ago. (29, 482). In the preface to this edition, p. 6, the author says: "This monograph follows closely the form of its first edition. The advances of the last few years have, however, been so many and important that nearly every chapter has been rewritten. Part I deals with crystal structure methods. As before, this portion of the book is not intended as a handbook: it seeks only to outline those procedures which the personal experience of the writer indicates as best suited to present-day structure determination. Part II is again concerned with results. The substances studied have become so numerous that they could be included within the allotted space only through a condensed treatment which forbids a thoroughly critical approach to the data upon many compounds. The same multiplicity of results has also prevented discussion of the many interesting studies of X-ray diffraction which do not lead to atomic positions. Though this second edition is thus somewhat more limited in scope than the first, it is intended to be complete within its narrower field. No work published in 1931 has been considered."

In Part I on the method of crystal analysis the chapters are entitled: introduction; the symmetry of crystals; some properties of X-rays; the interaction of X-rays and crystals; X-ray spectroscopy in crystal analysis; production and interpretation of the Laue photographs; X-ray powder spectroscopy; single crystal and powder spectrometry; the determination of crystal structures. In Part II on results of crystal analysis the chapters are entitled: introduction and structures of the elements; structures of the type RX; structures of the type RX_2; structures of the type R_2X_3 and of higher compounds R_mX_n; structures of the type $R_x(MX_3)_y$; structures of the type $R_x(MX_4)_y$; structures of the type $R_x(MX_4)$; the structures of hydrates and ammoniates and of miscellaneous inorganic compounds; structures of the silicates; structures of organic compounds. There is also a bibliography of crystal structure data.

"Perhaps the most important qualitative result of X-ray diffraction research is the realization that almost all solids are crystalline. This is true of most precipitates and colloids, whether of organic or inorganic origin. The only conspicuous exceptions to universal crystallinity are some low temperature decomposition products and also the glasses, whose behavior towards X-rays, like most of their other physical characteristics, is that of highly viscous liquids.

"The other great change in outlook brought about by X-ray studies has arisen from the observation that no molecules can be found in structures of most inorganic crystals. The habit of talking about ionic compounds is already leading us to forget that before the first interpretation of crystal structure, chemical molecules in solid NaCl or K_2SO_4 seemed as real to physical chemists as the O_2 and N_2 molecules in air. In contrast to these ionic crystals wherein the physical molecule is identical with the solid fragment, the chemical molecules of organic and other non-dissociable compounds are readily discerned in their structures. One of the most important contributions made by crystal analysis is its direct test of the correctness of both the general principles and the special details underlying structural chemistry. Although the relative difficulty of determining atomic positions in organic substances leaves most of this information yet to be acquired, a start has been made. Thus a sufficient number of aliphatic compounds have been examined to show the essentially tetrahedral character of the bonds about a carbon atom tied to four other atoms. Studies of hexamethyl benzene and of naphthalene and anthracene on the other hand bring out the planar character of the bonds of the benzene ring and the greater intensity of the aromatic carbon-to-carbon linkage. In accordance with this difference, the cyclohexane ring, as it occurs in its hexachloride for instance, is 'puckered' in a way that contrasts clearly with the flat benzene ring," p. 18.

"It is apparent from the preceding equations that the quantitative application of crystal reflection data to the determination of atomic positions depends in the first instance upon knowledge of the atomic scattering powers expressed in the quantities called F. It is convenient to distinguish two kinds of F—the reflection F"'s and atomic F's. The scattering powers of the individual atoms of a crystal under the conditions of a reflection are atomic F values; the composite of their several contributions, expressed by the structure factor, has been seen to measure the reflection F'. This reflection F' is directly established through accurate intensity observations. Though the scattering powers of individual atoms are as yet only incompletely known, a number of experimental studies have been made and theoretical interpretation has progressed far enough to provide information adequate for most of the practical requirements of crystal analysis," p. 96.

"As far as can now be seen the precise F-curve of an atom cannot be predicted in advance of a knowledge of the structure of the crystal to which it applies. This uncertainty has its origin in more than one cause. Thermal agitation modifies the effective electron distributions and with them atomic scattering powers. The reflecting power of an atom, like the number and position of its electrons, changes with the state of its chemical combination. The extent of this variation has not as yet been accurately determined but it is sure, for example, that F for chlorine in a chloride is measurably different from its scattering power in a chlorate or perchlorate. Atomic F-curves depend upon the wavelength of the X-rays used. Though absolute reflecting powers have been obtained only for the neighboring K-α lines of rhodium ($\lambda = 0.614$A) and molybdenum ($\lambda = 0.710$A), many relative reflecting powers, established with other radiations, outline the general course of this change. Atomic scattering varies but slightly for wave lengths far removed from critical frequencies, but suffers sharp and important fluctuations in their neighborhood. For a constant $\sin\theta/\lambda$ an atomic F steadily decreases as λ approaches its K-absorption limit from the short wave length side and then rises sharply with further increase in λ to a maximum located near the K-α doublet of the scattering atom. It is fortunate for the progress of crystal analysis that such approximate scattering powers as result from neglecting or making a more or less qualitative correction for these modifying factors are sufficiently good for most determinations of atomic positions," p. 97.

"Laue photographic data, prepared and analyzed in the manner that has been outlined, find their main use in deciding the symmetry and especially the correct unit cell of a crystal. The qualitative data from complicated planes, far more numerous than those obtained in other diffraction experiments, can be employed to select the correct cell with a certainty not achieved in any other fashion. The value of Laue comparisons in choosing the atomic positions in crystals with few parameters has been mentioned in the preceding paragraphs. Relatively few of these substances, however, remain to be investigated," p. 150.

"When a thin film of crystalline powder replaces a single crystal in the X-ray spectrograph a different pattern results. Provided the individual crystals of this powder are sufficiently numerous and are haphazardly oriented, some of them are in position to reflect from every atomic plane whose spacing exceeds a minimum fixed by the X-rays used. The series of diffraction lines thus produced by monochromatic X-rays constitutes a powder photograph. Since each line is composed of reflections from only a few particles, more energy is required to produce one of these photographs than to record other X-ray diffraction phenomena. Where it can be used, the powder method has two outstanding advantages. The more obvious is the ability to study crystalline materials which do not grow large single crystals. Of equal importance is the fact that most substances can be powdered in such a way as to reduce them to the ideally imperfect state. The simplicity and certainty with which the intensities of reflections from such crystals may be interpreted make them especially useful in structure determination," p. 151.

"Powder photographs have only a limited usefulness in studies of atomic positions. With substances of high symmetry their data can sometimes be used in a qualitative fashion to distinguish between possible arrangements. For very simple crystal comparison powder photographs against NaCl or some other standard provide an ideal way of obtain-

ing precise knowledge of cell dimensions. Otherwise powder photographs are valuable mainly for purposes of identification and to give photographic records of materials being measured with the spectrometer," p. 166.

"The absence of faces of low symmetry is not proof of high symmetry of atomic arrangement. It happens sometimes that even the symmetry of Laue patterns may seem higher than that of the substance producing them. Thus several cubic substituted ammonium chlorostannates are known which can scarcely be more than tetratohedral though their diffraction phenomena and face development seem completely holohedral. Many other less striking examples have been encountered.

"In addition to the criteria already mentioned, crystallographers have often made use of etch- and other solution-figures as indices of symmetry. The atomic arrangement found by X-ray methods to prevail within a crystal at considerable depths beneath its surface must be only one of several factors influencing the manner in which its faces are dissolved away; it is not surprising that several examples should already have been found wherein the etch-figure symmetry conflicts with that of well determined structures," p. 181.

"The sizes of the atoms in metals are given directly by their distances apart. At first it was supposed that positive ions were larger than negative ions possessing the same number of electrons. In reality an atom becomes successively smaller as it loses electrons and as the field within which its remaining electrons lie becomes more intense. For the same reason a negative ion is much larger, or more diffuse, than its neutral atom. When this was realized, ionic sizes could be calculated through the contacting of negative ions in a compound composed of large negative and especially small positive ions. Thus Landé's assumption that the size of the unit cell of LiI is fixed not by the contacting of Li^+ and I' ions but by the meeting of large I' ions provides a starting point from which the sizes of other monovalent ions can be calculated. The same ionic radii were arrived at by Wasastjerna from considerations of ionic refractivity and constitute the actual basis upon which the present extensive system of atomic 'size' has been developed.

"From what has already been stated it is evident that a different size must be assigned to an atom for each of its several valence states. Where, as in the alkali halides, the atoms are simple ions, they can be considered as essentially spherical. There is a wide departure from this symmetrical shape, however, in complex ions and in the union of large electronegative ions, such as iodine, with small and highly charged positive ions. In the carbonate group, for example, the oxygen-to-oxygen distance (2.18A) is much less than the sum of two oxygen radii (2.80A). This distortion, shown most conspicuously in such too close approaches of large electronegative atoms, is commonly called polarization.

"Size is not always the same even for a simple ion of constant valence. As might be expected, the effective radius of an ion becomes smaller the fewer the atoms of opposite charge surrounding it and the more intense its field. This effect of coördination number, as it is often called, is important when the number is less than six; the radii for a coördination number of eight are approximately three per cent greater than for one of six; for large numbers ionic radii are substantially constant," p. 190.

"In the alkali halides or in MgO the atoms are clearly ions, in the diamond and in organic compounds in general they probably do not bear electrical charges. It is apparent that all sorts of gradations exist between the purely polar bonds of the first and the nonpolar unions in the latter. It is equally sure that associated with these differences in atomic bonding go differences in atomic 'sizes.' This is illustrated by the phenomenon which has been called 'commensurability.' The extreme cases of purely polar and purely non-polar bonds are easily recognized but no satisfactory method is available for classifying the intermediate stages; hence for such crystals great care must be exercised in the use of information about atomic sizes.

"The concept of atoms as not more than moderately deformed spheres is of little value among the truly molecular compounds composed of non-ionized atoms. The majority of these substances are organic. They are difficult to treat partly because their carbon, oxygen, nitrogen and similar light atoms undoubtedly cannot be taken as spheres, and partly because the hydrogen atoms cannot be located. At the present time there is no

conclusive reason for believing that these hydrogen atoms, in an NH_3 or a CH_3 group for example, have positions which conform to the symmetry of the rest of the crystal and there are many indications that they are either randomly distributed in individual radicals or that the radical itself possesses a character of heat motion which gives it a shape equivalent to a random distribution. Under such circumstances the only practical procedure is to consider these groups and radicals as if they were single atoms of such a high degree of deformability that only their separations from other atoms within and without the molecule are significant. The distance between two adjacent methyl carbon atoms of a molecule, to choose a frequently met illustration, is close to the carbon-to-carbon distance in the diamond, 1.54 A; but between methyl groups not bound together by primary valence bonding, such as those of adjacent molecules, this distance seems always to be more than twice as great, ca 4.10 A. Some of these interatomic distances, which with care can be used in the same way as radii to help in structure determination, are mentioned in Chapter XX," p. 191.

"Crystals of HgO have a unit orthorhombic cell. The mercury atoms of its two molecules are in a body-centered array; on account of the overwhelming scattering power of mercury, oxygen positions have not been established. Though agreement upon the point is not unanimous it is apparent that red and yellow HgO have the same crystal structure," p. 221.

"The phenomena accompanying the production of so-called magnetic ferric oxide somewhat resemble those involved in oxidizing Sb_2O_3. When magnetite, Fe_3O_4, is oxidized under certain conditions an Fe_2O_3 is formed which remains strongly magnetic. The X-ray diffraction pattern of this ferric oxide is seemingly indistinguishable from that of the original Fe_3O_4. Space exists in the magnetic grouping for the oxygen atoms needed to produce Fe_2O_3, but the actual positions involved in such a substitution have not been definitely established. A similar produce is obtained by the oxidation of the spinel $CoFe_2O_4$," p. 258.

"Artificial spinels are notable for their ability to dissolve an excess of alumina. The patterns of such substances are said to differ very little from those of the pure compounds. If, as reported, the γ-form of Al_2O_3 gives spinel-like photographs, the alumina-rich preparations may be its solid solutions with the spinels themselves," p. 293.

The chapter on the structure of hydrates is rather a sad one. There is very little real information in it and what little there is is not presented for the benefit of the chemist. Fig. 232 purports to tell something about $(NH_4)_2CuCl_4.2H_2O$; but it is by no means easy to identify any of the atoms. In gypsum the two waters seem to be attached to the calcium, p. 314, while six waters are attached to nickel in $NiSnCl_6.6H_2O$, p. 316; but there is nothing to show where the five waters are in copper sulphate pentahydrate, p. 315.

"One of the most striking characteristics of silicates as a group is the variation from compound to compound in their silicon-oxygen ratios. Thus there exist not only ortho-silicates and metasilicates but pyrosilicates (Si_2O_7) and others showing a variety of compositions between SiO_2 and SiO_4. In combinations of oxygen with other elements, such as sulfur or chlorine, different ratios would be explained by differences in the valence of the combining element. As far as is known silicon is always tetravalent. X-ray analysis has made evident two reasons for the apparently variable combining power of this element. One is the fact that silicon always occupies the center of a tetrahedron of oxygen atoms; the second is the ability of these SiO_4 tetrahedrons to link up with one another by having oxygen atoms held in common. If SiO_4 groups are dispersed throughout the structure in the same way that SO_4 ions are distributed in a sulfate, the substance will be an ortho-silicate; in most other silicates oxygen atoms form part of two tetrahedrons.

"The several ways in which silicon and oxygen can conceivably be joined together in accordance with the foregoing principles offer a convenient means of classifying and grouping these minerals. Discrete groups can be of two sorts, simple SiO_4 tetrahedrons and definitely limited associations of a few tetrahedrons. A different linkage is provided by the pyroxenes, in which chains of groups extend without geometrical limit throughout the crystal. In the amphiboles these chains are double. If this doubling is repeated till an unlimited sheet of tetrahedrons is produced, the grouping probably possessed by the micaceous silicates will result," p. 322.

"The mineral *mullite*, $3Al_2O_3.2SiO_2$, with diffraction data which are almost identical with those of sillimanite, must have a very similar atomic arrangement. A cell equal in size to that of sillimanite would contain $3/2$ molecule, or $Al_9Si_3O_{19.5}$. This is to be compared with the four molecules, or $Al_8Si_4O_{20}$, within the sillimanite unit. It seems probable that the mullite cell is twice that of sillimanite but that the metal atoms have nearly the same positions in both except that a mullite aluminum replaces a sillimanite silicon atom. The necessary approximate identity of the oxygen positions in the two crystals is made possible by the fact that they differ in their oxygen content by only one part in 40. Replacement of silicon by aluminum, such as is assumed in an interpretation of this sort, is common among the more complicated silicates," p. 331.

"In mineralogy it is customary to classify a large number of metasilicates as pyroxenes. The following have powder patterns which show that their structures are diopside-like (**1925**, 271): hedenbergite $CaFe''(SiO_3)_2$, jadeite $NaAl(SiO_3)_2$, acmite $NaF'''(SiO_3)_2$ and the augites which are complex solid solutions of acmite and diopside. Wollastonite, $CaSiO_3$, has been given a monoclinic cell which is supposed to contain 12 molecules (Table I). Powder patterns show that the substances bustamite $(Ca,Mn)SiO_3$, pectolite $(Na,H)_2$-$Ca_2(SiO_3)_3$ and schizolite $(Na,H)_2(Ca,Mn)_2(SiO_3)_3$ are structural isomorphous with wollastonite. Measurements have also been published of the cell dimensions of the triclinic pyroxene-like minerals rhodonite and babingtonite. More work is needed to determine the true units of these substances and to establish any relationships they may have with one another," p. 346.

"Perhaps the most interesting feature of these amphibole structures, aside from their analogies with the pyroxenes, lies in the character of the silicate chains they possess. In the pyroxenes the silicate chains are single (Figure 256a); in the amphiboles they are doubled to have the appearance of Figure 256b. It is interesting to note that both the pyroxenes and the amphiboles show elongated growth along the direction of their c, or chain axes; where these chains are double, in the amphiboles, the bonds along c are so much more intense than in other directions that the crystals often appear as fibres. The immediate implication that the fibrous nature of all asbestos-like minerals finds its explanation in the existence of these chains is reinforced by the partial structure that makes chrysolite a composite of Si_4O_{11} chains and of brucite, $Mg(OH)_2$, elements. The crystal is monoclinic with a unit containing four molecules of a composition written $Mg_6(OH)_6Si_4O_{11}.H_2O$. In the suggested arrangement for which parameters have been assigned along the a and b, but not the c, directions these atoms are distributed according to the requirements of C^3_{2h}," p. 349.

"It is an obvious step from the double silicate chains of the amphiboles to an unlimited plane net of attached silicon-oxygen tetrahedrons. If chains of tetrahedrons make a mineral fibrous, crystals containing sheets should be platy and it is among the micas and similar substances that they may be expected. Complete data have not yet been published for any of these minerals but preliminary notices concerning the atomic arrangements prevailing in the micas, the alkaline earth or brittle micas and talc indicate that they are in fact built in layers. In talc these sheets have a balanced or zero valence within themselves and are bound together by stray forces. In mica and the chlorites, aluminum is thought to replace some of the silicon. The negatively charged layers that result are linked together by alkali atoms in the first case and by divalent ions in the brittle micas," p. 350.

"The concept of spinning atomic groups will help in understanding the essentially spherical symmetries of ammonium, ammonia and water groups as they occur in many crystals. The same idea probably would serve to explain why the photographs of KCN are those of a perfect NaCl grouping with no apparent evidence of separate carbon and nitrogen positions.

"Unlike some other long chain solids, such as fatty acids, no distinction exists among the simpler substituted ammonium halides between odd and even numbered carbon chains. A preparation of undecyl ammonium iodide was found to have two forms, the one that is isomorphous with the rest of the group being unstable and disappearing after two or three days. This may well represent the beginnings of differentiation into an odd and an even

series. Members of this isomorphous series form solid solutions with one another and undoubtedly the abnormal spacings of the heptyl ammonium iodide and some of the other chlorides and bromides listed in Table II are thus to be accounted for," p. 364.

"Hexamethylene tetramine, $C_6H_{12}N_4$, is one of the few organic substances whose structure may be taken as thoroughly established. It is cubic with a unit containing two molecules which have a minimum symmetry of T if the correct space group is T^4_d, or of T_d if it is T^3_d. Both groups lead to the following arrangement for the carbon and nitrogen atoms and hence no selection is possible between them," p. 389.

Wilder D. Bancroft

The Age of the Earth. *By Subsidiary Committee on the Age of the Earth. 25 × 17 cm; pp. vi + 487. Washington: The National Research Council, 1931. Price: $5.00.* This is the fourth volume in the Physics of the Earth Series. In the foreword, p. iii, the authors say: "It is generally agreed that more attention should be given to research in the middle ground betwen the Sciences. Geophysics—the study of physical methods of the planet on which we live—is a conspicuous instance of such a middle-ground science, since it shades off imperceptibly in one or another direction into the fields of physics, astronomy, geology, to say nothing of biology, with which the subject of oceanography is closely connected. Some branches of geophysics, such as meteorology, terrestrial magnetism, geodesy, and oceanography have long had a more or less independent existence, but it has become increasingly clear that these subjects, and many others, are all parts of geophysics. For various reasons, among which may be mentioned the development of geophysical methods in prospecting for oil and minerals, there has lately been a considerable development of interest in geophysics, but this development has not been matched by the publication in English of systematic treatises on the subject," p. iii.

The subject is presented under the general heads: summary of principal results, geochronology, or the age of the earth on the basis of sediments and life; age of the ocean; calculating the age of minerals from radioactivity data and principles; radioactivity and geological time; the age of the earth from astronomical data.

"At the beginning of the present century the problem of the age of the Earth was envisaged as requiring the reconciliation of three independent estimates, all of the same order of magnitude. These estimates were G. H. Darwin's, of 57 million years, based on the separation of the moon from the Earth; Lord Kelvin's, of 20-40 millions, based on the secular cooling of the globe; and Joly's, of 80-90 millions, based on the rate of accumulation of sodium in the world-ocean. To these should be added Helmholtz's estimate of 22 million years, based on the source of the sun's heat and its probable duration.

"Shortly after the opening of the century the discoveries of radioactivity destroyed the foundations on which the principal physical methods of estimating geologic time had previously rested. These discoveries, however, gave us methods based on atomic disintegration which soon indicated that geologic time is from 10 to 20 times as long as had been deemed probable from the estimates previously considered most trustworthy. These methods appear to involve far fewer assumptions than the geologic methods for measuring time, and the problem as we now see it is to reconcile estimates differing by a whole order of magnitude. In short, the radioactive evidence indicates that post-Cambrian time, i.e., from Ordovician onward is 450 million years, a span that is easily reconcilable with the geologic evidence, and that the age of the Earth is at least 2,000 million years, an estimate which, although not incompatible with the geologic evidence, is less readily reconcilable," p. 3.

"Some evidence is beginning to appear that the rates at which sediments were deposited in individual basins of sedimentation can be determined, and these rates will afford valuable checks on the determinations of geologic time that are based on atomic disintegration. Such measurements become possible where the strata show that they have been deposited by annual increments, each annual increment consisting of a summer and a winter lamina. The couplet, or annual layer, is called a varve. The difficulty in any given series of strata is to prove beyond question that the layers are annual—are really 'varves' in fact. By counting the varves in the Green River formation, Bradley has recently estimated that this

formation was deposited in a period lasting between 5,000,000 and 8,000,000 years. As the Green River formation appears to represent about one-third of Eocene time, this estimated great length of the Eocene, which is one of the shorter of the geologic time-periods, harmonizes well with the evidence from radioactivity," p. 4.

"Probably the phenomena of radioactivity that come oftenest to the attention of the geologist are the pleochroic halos. They are here discussed in detail and the problems that they evoke are fully discussed. Although the halos are known to be effects of alpha-particles ejected from radio-active inclosures in certain minerals, their actual mode of growth is not fully understood. Joly believes that they are of centripetal growth, but Schilling, working on the superbly developed halos in the fluorite of Wölsendorf, has demonstrated beyond much doubt that they are of centrifugal growth. Some halos have been formed by the cumulative effect of alpha-particles ejected at the rate of but one a year. In pleochroic halos we have a means of detecting radioactivity ten million times more sensitive than electrical methods. Halos cannot be used to determine the age of minerals, although Rutherford and Joly tried to do this for the biotite in a Devonian granite. But they had to guess the value of one factor in their calculations and, as has well been said, one might therefore as well guess the final answer. The fact of great import to the theory of age determination based on radioactivity that emerges from the study of the halos is that the rate of disintegration of 'uranium' and 'thorium' was the same in Pre-Cambrian time as it is now. This reassuring conclusion on the constancy of the rate of disintegration of uranium during geologic time is particularly the result of the work of Kerr-Lawson, who developed an improved technique in his investigation of the halos in biotite from a Pre-Cambrian pegmatite in Ontario," p. 8.

"The final proof that rates of radioactive disintegration have not varied during geological time is provided by pleochroic halos, to which more detailed consideration will be given in the next chapter. Thorium halos reveal no variation of radius with age, and, since there is a definite relation between the rate of disintegration of the atoms of an element and the range of the α-particles emitted, it follows that the rate of disintegration of thorium has not varied during geological time. In uranium halos a complication is introduced by the isotopic structure of natural uranium, a complication involving the possibility that in addition to uranium I and the probable actino-uranium there may be a still higher isotope so feebly radioactive that its disintegration could be detected only by its cumulative effects on the inner structure of uranium halos. However this may be, it is clear that Pre-Cambrian uranium halos in Canada show the same features in every significant respect as Devonian halos in Ireland and Tertiary halos from the Alps. So close is this parallelism that it may be used as evidence that the rate of disintegration of uranium I, the parent of the radium series, has been uniform over a period of the order 1,000 million years," p. 145.

"A very curious feature that accompanies or follows over-exposure is a bleaching of certain ring regions, the darkening first produced being 'reversed,' in the photographic sense of the term, by long-continued action of the α-rays. An exceptionally perfect example is illustrated by Joly, who shows a reversed uranium halo in a Pre-Cambrian biotite from Ytterby, Sweden. In juxtaposition Joly gives a Devonian halo from the Leinster granite. It is obvious that the dark bands of the normal halo have become bleached in the older example," p. 169.

"Until 1928 there was no laboratory production of reversal in biotite, but early in that year Jedrzejowski announced that he had succeeded in reproducing the phenomenon. He allowed α-rays from radon to act on a bright-green biotite plate. The change of tint produced was measured at intervals with a potassium photo-electric cell and an electrometer. The current was found to drop to a minimum as darkening progressed and then to rise again as reversal set in and more light was enabled to pass. The green biotite darkened rapidly to deep brown and continued application of the rays changed this relatively opaque tint slowly to a bright and more transparent yellow. Joly's forecast has thus been experimentally confirmed," p. 169.

"Poole correlates the gradual loss of water with the gradual darkening of the mica, and suggests that the original formation of the halo by α-rays from the nucleus is brought

about in a similar way. 'When α-rays enter either water or ice, they decompose it to a certain extent into hydrogen and oxygen. It seems highly probable that they would also decompose the water present in the biotite, which is apparently only very weakly held, and thus indirectly produce dehydration and its resultant darkening of the mica.' Experiments on the effect of heating biotite in coal-gas or hydrogen show that darkening proceeds just as usual and is therefore not due to external oxidation. In a later note Poole advocates the view that oxidation of the ferrous iron in the biotite is responsible for the halo darkening. In the heating experiments the water liberated is present as a gas well above its critical temperature, and under these conditions it would oxidize some of the ferrous iron to the ferric state, thus producing the observed darkening of the mica. In halo production the oxygen liberated from the decomposition of the water by α-rays would at once transform some of the ferrous iron of its environment into ferric," p. 188.

"It is not difficult to give a plausible explanation of a double period of granitization such as appears here to be implied. Such a phenomenon is already clearly recognized among the post-Bothnian granites and among the syntectonic and apotectonic phases of igneous activity associated with the Caledonian orogenesis. It is quite possible that when a geosynclinal column of sediments takes the place of part of the outer crust the total radioactivity of the column is increased. The depressed base of the sial will therefore tend to fuse and with the onset of orogenesis the magma will be squeezed upwards into the overlying sediments, now folded, plicated, and metamorphosed. This is the syntectonic phase. After the completion of orogenesis the new mountain column of sial will be practically solid from top to bottom, as all the former sial magma will have been squeezed upwards. The column will, however, be abnormally thick and the lower parts will sooner or later begin to fuse selectively as a result of the accumulation of heat of radioactive origin. The magma will work its way sideways and upwards, until the thermal distribution becomes stable. At a particular depth this constitutes the apotectonic phase. Thereafter there will be no further formation of magmas within the sial until its base is newly excited by thermal currents within the underlying substratum of sima," p. 281.

"Under laboratory conditions the rate of escape of helium from minerals always far exceeds the rate of production by radioactive change. Therefore the conditions under which the life of the minerals has been mainly passed, deep down in the Earth, where atmospheric agencies have no place, must be supposed more favourable to retention of helium, for otherwise the present accumulation could never have been formed. The observations here recorded leave little room for surprise that fossilised bones and other materials do not always contain as much helium as would be expected from their radioactivity and geological age," p. 394.

"Williams and Ferguson have drawn attention to the preferential permeability of silica glass to helium at various temperatures. Below 300°C hydrogen does not begin to diffuse through appreciably, but at 500°C the permeability to helium is nearly thirty times (about twenty-two times) as high as that to hydrogen. Other gases diffuse through silica glass much more slowly," p. 395. The permeability of silica glass may easily be measured at 180°.

<div align="right">*Wilder D. Bancroft*</div>

Chemische Bindung als elektrostatische Erscheinung. *By A. E. van Arkel and J. H. de Boer.* (*German edition by Li and W. Klemm*). *23 × 15 cm; pp. xx + 320. Leipzig: S. Hirzel, 1931. Price: 15 marks, bound 17 marks.* This book gives an account of the theory of ionic cohesion, based on Kossel's idea that atoms tend to lose or gain electrons in order to achieve the stable inert gas structure. In many directions the theory has been extraordinarily fruitful and has permitted of quantitative calculations of many physical properties, such as crystal and molecular energies, not formerly amenable to calculation. These advances are reviewed and a careful comparison is recorded of theoretical and experimental results. For this reason the book is rich in experimental material which considerably enhances its value.

In some cases the polarisation of atoms and ions is discussed at length. Due stress is laid on the effect of this polarisation on the shape of certain molecules, such as H_2O and NH_3,

and on its importance in determining whether the crystalline state of a substance is of the molecular, sheet or coordination type.

The main weakness of the book lies in the tendency of the authors to push the Kossel idea too far. The fervour of the disciples outruns the wisdom of the prophet. In discussing methane, for instance, it is assumed to be ionic and the only question to be settled is whether the hydrogens are negative or positive ions. It is finally decided that they are negative although in NH_3 they are considered to be positive.

The developments on the theoretical side during the last three or four years, which have led to a new understanding of the nature of chemical forces, are only briefly sketched in the closing pages of the book and find no place in the general scheme. None the less it is quite certain that the classical electrostatic picture of ions will be found in many cases to be a good approximation, and much of the theory of ionic binding given in this book (particularly that referring to ionic crystals such as NaCl) will stand. Used with discrimination, the book should be of interest and value to all those interested in molecular physics or chemistry.

J. E. Lennard-Jones.

The Dipole Moment and Chemical Structure. *Edited by P. Debye. Authorised translation by Winifred M. Deans. 23 × 16 cm; pp. x + 134. London: Blackie and Son, 1931. Price: 10 shillings.* This is an authorised and very pleasing translation of the papers given at the Leipzig conference of 1929; the German edition has already been reviewed in this JOURNAL. It thus makes available for English readers a number of interesting papers on the molecular beam method of measurement, dipole moment and velocity of reaction, the Kerr effect, and other problems of physics and chemistry which have been illuminated by our growing quantitative knowledge of the electrical asymmetry of molecules. The wide range of these problems is very striking; at the same time it is clear from these papers that much remains to be done as regards the accuracy with which the dipole moments can be determined and that some of the earlier generalisations, e.g. the constancy of moment in homologous series, need serious modification.

This volume should interest workers in the field of molecular structure as much for the emphasis which it lays on the gaps in our knowledge as for the advances which it records.

S. Sugden.

Theoretische Grundlagen der organischen Chemie. *By W. Hückel. Vols. I and II. 22 × 15 cm; pp. Vol. I, ix + 410; Vol. II, iv + 252. Leipzig: Akademische Verlagsgesellschaft, 1931. Price: Vol. I, 24 marks; Vol. II, 20 marks.* In some respects the new work is disappointing: it claims to be a treatise on the theoretical principles of organic chemistry; yet no use at all is made of the group of theoretical principles (electro-chemical), now well established by British and American work, which would have been of more value to the author than any other for collating the wealth of fact which his book contains. On the other hand there are several reasons why the book forms a valuable addition to our literature; and the most important of these is that it introduces the student of organic chemistry to lines of physical evidence regarding structure and reactivity, of the existence and power of which conventional training often leaves him unaware.

The book opens with a survey of the electronic theory of valency. The outline is excellent and the reviewer's only criticism is that for all the use that is made of it subsequently it almost might have been omitted. It stands isolated; it might, in its modern development, have formed a cement to weld together the whole of the remainder of the book. A chapter on stereochemistry follows, and the student is then introduced to co-ordination compounds and to free radicals. These subjects are completely detached; there is no common underlying theory. Prototropy is considered and the relation of triad tautomerism, ring-chain tautomerism and reversible additive synthesis is traced, curiously without reference to the literature of these ideas. Anionotropy is discussed, but not as the counterpart of prototropy; indeed the theory of the subject is wholly omitted. The Wagner-transformation is then dealt with, and considerable space is devoted to the obsolete cyclic theory; the modern

general theory is not mentioned. In the chapter on addition reactions the additions of Br_2, HOCl and HCN are all represented as reactions of the molecule, and in regard to the mechanism of both to simple and conjugative additions the decisive work of the present century is wholly neglected. The reactions of unsaturated and aromatic compounds are discussed mainly from the view-point of Thiele's theory of partial valencies. On the whole, Volume 1 is somewhat disappointing.

Volume 2 commences with an extremely interesting chapter on the relation of molecular electric moments to constitution. This is probably the best existing essay on this topic with the exception of the new book "Dipole Moment and Chemical Structure" edited by Debye. The student is then shown the molecular significance of the phenomena of the polarisation and dispersion of scattered light and of electric double refraction. One wishes that this general explanation of the anisotropy of polarisability had been followed by a more thorough consideration of its relation to constitution since suitable data exist, though they have not yet been adequately collected and discussed from this point of view. The first half of Volume 2 also contains a thoroughly up-to-date chapter on cohesion and a very interesting discussion on molecular array in liquids. The whole of this part of Volume 2 is well worth careful study by both teachers and students. The second part of Volume 2 is devoted to a consideration of reaction velocity in relation to constitution. The opportunity is taken to explain the significance of critical energies and action constants, but no adequate treatment of solvent-effects is included, and to some extent this section falls short of expectation in the same directions as Volume 1.

Advances on previous treatment cannot be expected to pervade the whole of a work of such wide scope as that under review. Its principal novelties as an educational instrument are contained in the first half of Volume 2. The rest of the work will be read mainly as an interesting reflexion of the modern German outlook on the problems of organic chemistry.

C. K. Ingold

Bernstein. *By Leopold Schmid.* *25 × 18 cm; pp. vii + 102. Dresden: Theodor Stein-kopff, 1931. Price: 7 marks.* This section of the Doelter-Leitmeier's Handbuch der Mineralchemie deals in considerable detail with the prehistorical and historical aspects of amber and with the occurrence and distribution of this valuable natural resin. Mention is made of the various geological strata in which amber is found and in this connexion the solid inclusions in amber are of considerable palaeontological significance.

Amber is collected on the coasts of the North and Baltic Seas and especially on the promontory of Samland in East Prussia. Further inland in these localities it is obtained by mining.

The manifold past and present uses of amber are described, some of which are now only of historical interest, such as its employment in medicine. The physical and chemical properties of amber are described and special reference is made to its electrical properties. Among its chemical characteristics are the derivation of succinic acid, amber oil and amber colophony and of special interest to chemists is the separation of its components into fractions soluble and insoluble in alcohol.

Methods are outlined for distinguishing between true amber and its imitations and many analytical figures are given of various species of amber. There is, however, no mention of the fact that whereas bakelites have approximately the same carbon content as ambers (78 to 80%) yet the synthetic phenol-formaldehyde resins have much lower hydrogen contents (6.5%) than those of the true ambers which are round about 10%.

The closing section of the treatise describes briefly some thirty-five fossil resins which are allied to the true resin (succinite) of East Prussia but there is no mention of the amber found on the coasts of East Anglia.

Each main section contains a full bibliography and the book may be recommended to all interested in amber whether industrially or from a more general viewpoint.

G. T. Morgan
E. L. Holmes

Laboratory Manual of Physical Chemistry. *By Albert W. Davison and Henry S. van Klooster. Second Edition. 23 × 15 cm; pp. xi + 237. New York: John Wiley and Sons; London: Chapman and Hall, 1931. Price: 12 shillings, 6 pence.* This practical text-book has many merits and clearly bears the imprint of considerable laboratory teaching experience. The range of experiments is wide; the only notable omissions are experiments on polarisation and oxidation-reduction potentials. The arrangement of each experiment is eminently practical. The instructions for their performance are a model of lucidity and detail.

There is a certain tendency to employ rather "specialist" apparatus in cases where some teachers might prefer to use cruder, simpler apparatus made from standard laboratory equipment. For example the Cottrell and the Eykman boiling-point apparatus are used where some might prefer a Landsberger apparatus made by the student himself. It is possible, too, that the average student would learn more by the use of an inexpensive form of Pulfrich refractometer simpler in principle than the Abbe instrument described.

The text follows the practice, commoner in America than Europe, of leaving the student little opportunity to make mistakes and correspondingly little opportunity to exercise his initiative. The book itself is made up with graph-paper, blank-pages and a space individually arranged for the tabulation of the observations made in each experiment; it thus serves the double purpose of text-book and note-book. It is a matter of personal opinion whether such assistance at every point does more good by eliminating wasted time and unsuccessful experiment than it does harm by discounting the self-reliance of the student. Those who subscribe to the "fool-proof" theory will find the present volume admirable in every respect; the dissenters are likely to find many of its details of technique useful.

J. H. Wolfenden

Gmelins Handbuch der anorganischen Chemie. *Edited by R. J. Meyer. Eighth edition. System-number 58. Cobalt. Part A, No. 1. 25 × 17 cm; pp. 220. Berlin: Verlag Chemie, 1931. Price: 34 marks (subscription price 30 marks).* The present section includes part of the chemistry of cobalt and deals with the history, occurrence, production of compounds from ores and intermediate products, the preparation and properties of metallic cobalt, analytical methods, and alloys. The treatment follows the usual lines of the whole work and both the information and literature references are complete and up to date. Cobalt plating and stellite are included and the magnetic and analytical properties are dealt with in some detail. The section on alloys includes phase rule diagrams in most cases.

J. R. Partington

Lehrbuch der Radioaktivität. *By Georg v. Hevesy and Fritz Paneth. Second German edition, completely revised. 23 × 16 cm; pp. xii + 237. Leipzig: J. A. Barth, 1931. Price: 22 marks; bound 24 marks.* This is the second edition of the book which was published in Germany in 1922. An English translation, by Dr. Lawson, was published by the Oxford University Press in 1926, and it has since become generally known as one of the best books on the subject that has appeared. The authors are both by origin physical chemists, who have carried out researches in radioactivity in Great Britain, and have made notable contributions to its development. The use of radio-elements as indicators of common elements isotopic with them is due to them and has had numerous applications not only of a practical character, but also to the extension of electrochemical theory to ranges of concentration below the lowest attainable by ordinary methods. The method of separation of inactive isotopes by unidirectional distillation and a share in the discovery of hafnium belongs also to the first-mentioned of the two authors.

The book was the first to separate the didactic from the historical aspects of radioactivity and to be a text-book of the subject rather than an account of the original investigations, the historical development being relegated to the final chapter. The authors claim that a text-book of chemistry does not begin with the misconceptions of the alchemists, and although the analogy is, perhaps, not a very happy or accurate one, we have to admit that, however much the subject loses by being systematised into text-book form, the change is as inevitable as death. Rather we must bewail how much ordinary chemistry text-books lose by the necessity for being systematic instead of being concerned with the comparatively few discoveries that really count.

In 26 short chapters the book attempts to cover the very wide field both on the physical and the chemical sides, and, if the treatment is necessarily condensed, how much more so is the attempt to get it into one chapter, which is all that most books on physical chemistry can spare. As a supplement to the reading of the ordinary physical chemistry student and as dealing with something that is at once both chemistry and physics rather than a peculiar hybrid, the book is in every way warmly to be commended.

The subjects revised in the new edition are, chiefly, those dealing with the structure of the atom, radioactive indicators, the precision measurements of isotopic masses and the geological and cosmical implications of radioactivity. The chapter on radioactive indicators has been rewritten to meet the needs of those who require to use these methods without otherwise being concerned with radioactive technique. We note the inclusion of the Pauli exclusion principle to the interpretation of the Periodic Table and some of the more recent views that have been ventilated as to the nucleus. If the reader makes nothing of them that is not the fault of the book, but his own if he expected anything else. The book is also brought up-to-date as regards the age of minerals, pleochroic halos and the cosmical radiation.

Frederick Soddy

Chemie und Chemische Technologie tierischer Stoffe. *By Georg Grasser. 23 × 14 cm; pp. 272. Stuttgart: Ferdinand Enke, 1931. Price: 16 marks; bound 17.60 marks.* It is debatable whether much is to be gained by publishing volumes which aim at presenting comprehensive but superficial surveys of highly specialised fields of applied science. If such books are produced the reader is entitled to expect that reasonable care has been taken to present an accurate and up-to-date picture of the subject. A considerable proportion of this volume is taken up with a general account of the chemistry of the substances which enter into the composition of animal tissues. It would have been out-of-date thirty years ago. Here and there some effort to bring in modern work has been made, often with most unhappy results, as, for example, when we read (p. 159) that thyroxin *is* trihydro-tri-iodo-oxy-β indolpropionic acid, but that a difficult synthesis has led to the production of a compound $C_{15}H_{11}O_4N_{14}$ (Harrington's constitutional formula is given) which has the same physiological action as the thyroid gland!

It is impossible to read the book without gaining the impression that both in the scientific and practical fields of animal chemistry the author has failed to keep fully abreast with the important developments of the past decade. It may be significant that almost all literature other than German is ignored.

J. C. Drummond

The Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals. *By Alexander N. Winchell. Second edition. 23 × 15 cm; pp. xvii + 403. New York and London: John Wiley and Sons, 1931. Price: $5.00.* The first edition of this book appeared as No. 4 of the University of Wisconsin Studies in Science. The present edition includes, in addition, a section on Principles and Methods, largely taken from the author's "Elements of Optical Mineralogy, Part I," and a chapter on the Universal Stage, by R. C. Emmons. Over half of the work consists of optical descriptions of inorganic salts, and a tabulation of their optical properties for purposes of identification.

The substances included are limited to those that have been described fairly completely. This means that a number of common salts, for which only a few optical properties are known, are not mentioned or listed in the determinative tables. On the other hand, the author's use of the term "artificial minerals" is not to be taken as indicating that compounds known only in the laboratory are excluded. The descriptive portion of this work should be invaluable to any chemist who has occasion to identify or compare inorganic salts by means of the microscope. It is by far the most complete collection of optical descriptions of such materials, and the arrangement and determinative tables add greatly to its usefulness.

As regards the discussion of methods and theory, its tone is more mineralogical than chemical. The physical chemistry of crystals is hardly touched upon, and it is rather surprising to find crystals defined as bodies "bounded by smooth surfaces" and having their atoms arranged in a definite and regular order.

Crystal aggregates, submicroscopically crystalline materials, factors governing crystal habit and growth, and especially methods of preparation of crystals for study might well have been discussed at greater length in a book that will be used primarily by chemists. The "double variation method" of refractive index determination, that depends on temperature control as a means of altering the refractive index of the liquid standard over a considerable range, is very clearly presented, as are the other more common procedures for determining optical constants of doubly refractive materials.

The reader is referred to "Elements of Optical Mineralogy, Part I" for a discussion of interference figures and observations in convergent polarized light. This is rather anomalous, for if one is to use the tables and descriptions he should be able to obtain and interpret interference figures, even from small grains; if the present work has to be supplemented by this other book, Part I is largely duplication.

The numerous diagrams of ideal crystals (in clinographic projection) and of optical orientations are a welcome addition, as an aid to the printed descriptions and in summarizing the variations of properties with composition in isomorphous series.   *C. W. Mason*

Veröffentlichungen aus dem Kaiser-Wilhelm-Institut für Silikatforschung in Berlin-Dahlem. *Vol. IV. 26.5 × 19 cm; pp. 452. Brunswick: Friedrich Vieweg and Sohn, 1931. Price: 38.50 marks.* Prof. Eitel states in his preface to this volume that the preliminary work of the Institute in devising experimental methods has now progressed so far that more rapid advances in their practical application are now possible. The aim of the investigators has therefore become more definitely technological, and by collaboration with manufacturing firms it is hoped to attempt the solution of problems which call for greater resources than those of a research laboratory. The new volume contains three papers by W. M. Cohn on the measurement of coefficients of expansion at high temperatures, up to 1400°. A very full review of the literature on the subject is included. An absolute method has been used to determine the properties of the material used for reference, and the apparatus is described by means of which these materials have been studied and used in the comparative method. The auto-collimating telescope is used in both forms of apparatus, and a photographic method of recording has been devised. For temperatures up to 900° silica glass has been found to be satisfactory as a standard, above that temperature Marquardt mass is used, and its coefficient has been determined. The method has been applied to various ceramic masses, and in particular to commercial zirconia. This refractory proves to have a much higher coefficient than has been generally supposed, being comparable with that of the glasses. Zirconia glass has been prepared, but too late to be included in the volume. The commercial forms of zirconia have constituents which show various space lattices. A compound $Mg_2Zr_3O_8$ is usually present, and has a cubic lattice, unchanged by heating to 1400°. The monoclinic lattice of ZrO_2 changes at about 1000° to a tetragonal lattice, the change showing marked hysteresis on cooling, when the sudden expansion sets up severe stresses. The high temperature transformations are not readily reversible. Above 1900° a new lattice is formed, either trigonal or pseudo-hexagonal rhombic, and this form undergoes a transformation, also accompanied by hysteresis, at about 500°, but this does not involve any considerable change of volume.

Three papers by W. Eitel and B. Lange deal with the absorption of light by coloured glasses. For this purpose the photo-electric cell is found useful, and this has been applied to the examination of transparent minerals in microscopic sections by means of an eyepiece in which the photo-electric cell replaces the upper lens. The same apparatus is used for the exact measurement of pleochroism, using monochromatic light.

The structure of β-alumina is described in a paper by W. L. Bragg, C. Gottfried and J. West, in a paper reprinted from the Zeitsch. Krist., and the X-ray structure of complex cyanides is described in detail by G. Nagelschmidt. The range of subjects considered is an indication of the scope of the Institute.   *C. H. Desch*

Gmelins Handbuch der anorganischen Chemie. *Edited by R. J. Meyer. Eighth edition. System-Number 29. Strontium. 25×18 cm; pp. xviii + xii + 239. Berlin: Verlag Chemie, 1931. Price: 41 marks (Subscription price 36 marks).* The present volume of the new Gmelin contains what seems to be a complete account of the chemistry of strontium, the literature being taken into account to 1 August, 1931. It follows the lines of previous parts and gives very detailed literature references, including patents. The metal can be obtained by electrolysis of fused salts and is silver white. It crystallises in the face-centered cubic system. The spectra are very fully dealt with, including the displacement of lines in the spark spectrum by pressure. The electrochemical properties follow. The compounds of strontium are completely covered, the physical and physiochemical data being tabulated in convenient form, and there are several phase rule diagrams. The evidence of the existence of subhalides from spectrum data is fully described. There does not appear to be any section on the analytical chemistry of strontium.

J. R. Partington

Outlines of Theoretical Chemistry. *By Frederick H. Getman. Fifth edition revised and largely rewritten by Farrington Daniels. 23 × 15 cm; pp. ix + 643. New York: John Wiley and Sons, 1931. Price: $3.75.* The choice of Professor Daniels to revise and bring up to date this popular text book of physical chemistry has indeed been a happy one for the new edition achieves in large measure the aims set in its preface. "To introduce recent advances without offending old friends who cherish the foundations of a successful past; to keep pace with present tendencies toward the mathematical viewpoint without driving away students who are inadequately prepared; and to sift out the permanent from the trivial are the privileges and responsibilities of this revision.

"The first revisions of a book can be made by addition, but there comes a time, as in the present case, where for every addition there must be a corresponding subtraction.

"Approximately one-third of the book has been changed. The chapters on Elementary Thermodynamics, Kinetics, Photochemistry, and Atomic Structure have been rewritten. The arrangement of chapters has been left unchanged except that two new chapters have been added, one on Chemical Thermodynamics using the notation of G. N. Lewis, and one on an Introduction to Quantum Theory. These fields have now become so important that even elementary students should have some acquaintance with them. The first half of the book has been made simpler, the last half somewhat more advanced. Models and mechanisms have been used freely to help in comprehending new subjects, but they are to be discarded without prejudice when outgrown," p. vii.

"One of the greatest helps in the discovery of hypotheses and in the practical application of theoretical chemistry is mathematics. In recent years there has been a decided trend toward more extensive use of mathematics in chemistry, and the chemist has seen several of his own problems solved by physicists and mathematicians who have been led to successful hypotheses through their ability to express the experimental facts in precise mathematical terms," p. 2.

"The formulas for electrode potentials have been developed in earlier sections through the concepts of thermodynamics and the simple relation between free energy and the mass law. They have been made exact formulas by using *activities* which are defined so as to make the formulas exact. Such a development is useful and logical, but as in all thermodynamical calculations it gives us no insight into the mechanism of the process," p. 443.

The new edition is a worthy member of the series and should enjoy wide acceptance. It mirrors clearly the new things and there remains only the question as to whether an emphasis on such matters is of more value in teaching students the outlines of theoretical chemistry than is greater attention to the more familiar and better digested parts of the subject. The interest and value of these new sections is not discounted by remarking that many of the older sections will have a more immediate and practical value to students who enter the field of physical chemistry through this book. A fair balance of these factors has been achieved and the book is recommended.

Herbert L. Davis

RELATIONS BETWEEN FUNDAMENTAL PHYSICAL CONSTANTS

BY J. E. MILLS

While engaged in an investigation of attractive forces the author calculated some functions involving basic physical constants which would not be calculated from the point of view usually adopted. It was found that certain similar numbers resulted in the most unexpected manner. For example:—

$$\frac{\pi\sqrt{1846.8}\,G}{\epsilon} = 18861; \quad \frac{c^2}{v^2} = 18850; \quad 3\pi Gc = 18829; \quad \frac{\epsilon^2}{1846.8h} = 18818$$

$$1/2\pi c = 0.53088 \times 10^{-11}; \quad \epsilon/m_0 = 0.53035 \times 10^{18}; \quad a = 0.53084 \times 10^{-8};$$

$$4\pi\,1846.8^2 = 42.859 \times 10^6; \quad h^2 = 42.863 \times 10^{-54}; \quad \mu v^2 = 42.861 \times 10^{-12};$$

$$\epsilon = 4.770 \times 10^{-10}; \quad v^2 = 4.7681 \times 10^{16}; \quad \frac{h^2}{(2\pi\epsilon)^2} = 4.7719 \times 10^{-36}$$

For the constants and symbols used see Table I.

TABLE I

Symbols and Constants

π = Geometrical constant	3.14159	
c = Velocity of light	2.99796 $\times 10^{10}$ cm sec^{-1}	
h = Planck's constant	6.547 $\times 10^{-27}$ erg sec	
m_0 = Mass electron	8.994 $\times 10^{-28}$ grams	
m_p = Mass proton	1.6610 $\times 10^{-24}$ grams	
ϵ = Electronic charge	4.770 $\times 10^{-10}$ absolute es units	
G = Gravitation constant	6.664 $\times 10^{-8}$ cm^3 gr^{-1} sec^{-2}	
τ = G. N. Lewis temperature unit = 1/k	7.289 $\times 10^{15}$	
N = Avogadro's number	6.064 $\times 10^{23}$ mole $^{-1}$	
$N\,m_0$ = Atomic weight of electron	5.454 $\times 10^{-4}$	
$N\,m_p$ = ” ” ” proton	1.0072346	
H = ” ” ” hydrogen	1.00778	
He = ” ” ” helium	4.00216	
O = ” ” ” oxygen	16.000	
μ = Reduced mass = $\dfrac{m_p m_0}{m_p + m_0}$	8.9891 $\times 10^{-28}$ grams	
mp/m_0 = Ratio mass proton to mass electron 1846.8		
M_{H_e} = Loss of mass in formation of helium	4.776 $\times 10^{-26}$ grams.	
T_0 = Ice point, absolute	273.18°C	
A_n = Normal atmosphere	1.013250 $\times 10^6$ dynes cm^{-2}	
V_n = Gram molecular volume	22.4141 $\times 10^3$ cm^3 mole^{-1}	

TABLE I (Continued)

R = Gas constant = $\dfrac{A_n V_n}{T_o}$ 8.3136×10^7 erg deg^{-1} mole^{-1}

k = Boltzmann constant = R/N = $1/\tau$ 1.3710×10^{-16} erg deg^{-1}

α = Fine structure constant   = $\dfrac{2\pi\epsilon^2}{hc}$ 0.7284×10^{-2}

β = Specific heat constant   = h/k 4.7753×10^{-11} sec deg

F = Faraday = $N\epsilon$ 2.89253×10^{14} es

v = Velocity of reduced mass in first Bohr orbit = $\dfrac{2\pi\epsilon^2}{h}$ cms/sec

a = Radius of first Bohr orbit   = $\dfrac{h^2}{4\pi^2\epsilon^2 \, \mu}$ cms

ω = Period of reduced mass, first Bohr orbit   = $\dfrac{\mu}{h}\left(\dfrac{2\pi\epsilon^2}{h}\right)^2$ sec

E_k = Kinetic energy of reduced mass,
          first Bohr orbit   = $\dfrac{\mu}{2}\left(\dfrac{2\pi\epsilon^2}{h}\right)^2$ ergs

R_H = Rydberg constant for hydrogen
          (Spectroscopic value of constants should
          be used)   = $\dfrac{\mu}{2hc}\left(\dfrac{2\pi\epsilon^2}{h}\right)^2$

ν = Wave frequency
λ = Wave length of light in cms per sec.
$\bar{\nu}$ = Wave number   = ν/c

Atomic weights are from Aston. The values of the other constants are taken mainly from Birge: Phys. Rev. Sup. **1**, 1 (1929).

As more and more functions were calculated it became evident that, ignoring the decimal point, nearly all of the functions calculated fell into a comparatively few series of figures. These series of functions and their reciprocals are given in Tables II-XIV.

TABLE II

		Functions related to c	Reciprocals
1	c	2.99796×10^{10}	$.33356 \times 10^{-10}$
2	3	3.0000	$.33333$
5	$\left(\dfrac{\epsilon}{m_o}\right)^{1/12}$	2.9995×10	$.33339 \times 10^{-1}$
5	$\dfrac{m_o}{2\pi\epsilon}$	3.0009×10^9	$.33323 \times 10^{-9}$
6	$\dfrac{1}{2\pi a}$	2.9981×10^7	$.33354 \times 10^{-7}$
7	$\dfrac{c^2}{2\pi v^2}$	3.0000×10^3	$.33333 \times 10^{-3}$
8	$\dfrac{h^2}{2\pi\epsilon^2}$	2.9982×10^{-35}	$.33353 \times 10^{35}$

<p style="text-align:center">TABLE II (Continued)</p>

		Functions related to c	Reciprocals
9	$\dfrac{c^2}{2\pi\epsilon}$	2.9989×10^{29}	$.33346 \times 10^{-29}$
10	$\dfrac{c^4}{2\pi h^2}$	2.9995×10^{94}	$.33339 \times 10^{-94}$
11*	$\dfrac{\sqrt{1846.8G}}{2\epsilon}$	3.0019×10^{3}	$.33312 \times 10^{-3}$
12	$\sqrt{m_0}$	2.9990×10^{-14}	$.33344 \times 10^{14}$
13	$2\pi\epsilon$	2.9971×10^{-9}	$.33366 \times 10^{9}$
14	$\dfrac{3Gc}{2}$	2.9967×10^{3}	$.33370 \times 10^{-3}$
24*	$\dfrac{\epsilon^3}{1846.8\ hc}$	2.9942×10^{-16}	$.33398 \times 10^{16}$
25	$\sqrt{\pi\sqrt{1846.8G}}$	2.9995×10^{-3}	$.33339 \times 10^{3}$
37*	$\dfrac{1}{2 \times 1846.8\ m_0}$	3.0102×10^{23}	$.33220 \times 10^{-23}$

<p style="text-align:center">TABLE III</p>

		Functions related to c^2	Reciprocals
1	c^2	8.9878×10^{20}	$.11126 \times 10^{-20}$
2	3^2	9.0000	$.11111$
5*	$\left(\dfrac{m_0}{2\pi\epsilon}\right)^2$	9.0054×10^{18}	$.11104 \times 10^{-18}$
6	$\left(\dfrac{1}{2\pi a}\right)^2$	8.9886×10^{16}	$.11125 \times 10^{-16}$
7	$\left(\dfrac{c^2}{2\pi v^2}\right)^2$	9.0000×10^{6}	$.11111 \times 10^{-6}$
8	$\left(\dfrac{h^2}{2\pi\epsilon^2}\right)^2$	8.9892×10^{-70}	$.11124 \times 10^{70}$
9	$\left(\dfrac{c^2}{2\pi\epsilon}\right)^2$	8.9934×10^{58}	$.11119 \times 10^{-58}$
11*	$\dfrac{1846.8G^2}{4\epsilon^2}$	9.0114×10^{6}	$.11097 \times 10^{-6}$
12	m_0	8.9940×10^{-28}	$.11119 \times 10^{28}$
13*	$(2\pi\epsilon)^2$	8.9825×10^{-18}	$.11133 \times 10^{18}$
15*	$\dfrac{\sqrt{1846.8}}{\epsilon}$	9.0093×10^{10}	$.11100 \times 10^{-10}$
16*	$\dfrac{1}{\sqrt{1846.8G}}$	9.0139×10	$.11094 \times 10^{-1}$
24*	$\dfrac{\epsilon^3}{1846.8h}$	8.9762×10^{-6}	$.11140 \times 10^{6}$
25	$\pi\sqrt{1846.8G}$	8.9969×10^{-6}	$.11115 \times 10^{6}$

TABLE IV

		Functions related to c^4	Reciprocals
1*	c^4	80.780×10^{40}	$.12379 \times 10^{-41}$
2*	3^4	81.000	$.12345 \times 10^{-1}$
8	$\dfrac{\epsilon}{hc^2}$	81.064×10^{-6}	$.12336 \times 10^{5}$
12*	m_0c^2	80.836×10^{-8}	$.12371 \times 10^{7}$
15*	$\dfrac{1846.8}{\epsilon^2}$	81.168×10^{20}	$.12320 \times 10^{-21}$
16*	$\dfrac{1}{1846.8G}$	81.255×10^{2}	$.12307 \times 10^{-3}$
21	$\dfrac{h}{m_0c^2}$	80.991×10^{-22}	$.12347 \times 10^{21}$
46	$\dfrac{\sqrt{1846.8}\ m_0}{\epsilon}$	81.024×10^{-18}	$.12342 \times 10^{17}$

TABLE V

		Functions related to c^6	Reciprocals
1*	c^6	$.7260 \times 10^{63}$	1.3773×10^{-63}
2	3^6	$.7290 \times 10^{3}$	1.3717×10^{-3}
3	$\dfrac{1}{\sqrt{6\pi}}$	$.7284 \times 10^{-1/2}$	$1.3729 \times 10^{1/2}$
4	$\dfrac{1}{\sqrt{2\pi c}}$	$.7286 \times 10^{-11/2}$	$1.3725 \times 10^{11/2}$
5	$\sqrt{\dfrac{\epsilon}{m_0}}$	$.7283 \times 10^{9}$	1.3731×10^{-9}
6	$\sqrt{a}$	$.7286 \times 10^{-4}$	1.3725×10^{4}
7	$\dfrac{v}{c} = \alpha$	$.7284 \times 10^{-2}$	1.3729×10^{2}
8	$\dfrac{\epsilon}{h}$	$.7286 \times 10^{17}$	1.3725×10^{-17}
9	$\dfrac{\sqrt{\epsilon}}{c}$	$.7285 \times 10^{-15}$	1.3727×10^{15}
10	$\dfrac{h}{c^2}$	$.7284 \times 10^{-47}$	1.3728×10^{47}
11	$\sqrt{\dfrac{\epsilon}{\pi\sqrt{1846.8}\ G}}$	$.7281 \times 10^{-2}$	1.3733×10^{2}
12	$\dfrac{1}{\sqrt{2\pi\sqrt{m_0}}}$	$.7285 \times 10^{13/2}$	$1.3727 \times 10^{-13/2}$
13	$\dfrac{1}{2\pi\sqrt{\epsilon}}$	$.7287 \times 10^{-4}$	1.3723×10^{4}
14	$\dfrac{1}{\sqrt{3\pi Gc}}$	$.7288 \times 10^{-2}$	1.3721×10^{2}
17	$\sqrt{3\pi}$	$.7280 \times 10^{5/8}$	$1.3736 \times 10^{-5/8}$

TABLE V (Continued)

		Functions related to c^6	Reciprocals
18	$\dfrac{3}{2\pi h}$	$.7293 \times 10^{26}$	1.3712×10^{-26}
19*	$\tau = 1/k$	$.7294 \times 10^{16}$	1.3710×10^{-16}
20*	$\dfrac{m_{He}}{h}$	$.7294 \times 10$	1.3709×10^{-1}
21	h/m_0	$.7279 \times 10$	1.3737×10^{-1}
22	$\dfrac{(2\pi\epsilon^2)^2}{h^3}$	$.7283 \times 10^{43}$	1.3731×10^{-43}
23	$\dfrac{1}{2\pi 1846.8}\sqrt{\dfrac{\epsilon}{G}}$	$.7291 \times 10^{-9/2}$	$1.3715 \times 10^{9/2}$
35	$\dfrac{\epsilon^{\frac{1}{2}}}{m_0^{\frac{1}{4}}\,c^{\frac{1}{2}}}$	$.7284 \times 10^{-3}$	1.3729×10^{3}

TABLE VI

		Functions related to c^8	Reciprocals
1*	c^8	6.5254×10^{83}	$.15324 \times 10^{-83}$
2*	3^8	6.5610×10^{3}	$.15242 \times 10^{-3}$
7	vc	6.5463×10^{18}	$.15276 \times 10^{-18}$
8	$\dfrac{\epsilon c^2}{h}$	6.5480×10^{37}	$.15272 \times 10^{-37}$
9	$\sqrt{\epsilon c}$	6.5476×10^{5}	$.15273 \times 10^{-5}$
10	h	6.547×10^{-27}	$.15274 \times 10^{27}$
29	$\omega = 2R_H c$	6.5467×10^{15}	$.15275 \times 10^{-15}$
30	$\dfrac{(4\pi\epsilon)^2}{c}\sqrt[3]{\dfrac{8\pi^5}{15}}$	6.5497×10^{-27}	$.15268 \times 10^{27}$
40*	$\sqrt[4]{1846.8}$	6.5557	$.15254$

TABLE VII

		Functions related to c^{10}	Reciprocals
1	c^{10}	5.8649×10^{104}	$.17050 \times 10^{-104}$
2	3^{10}	5.9049×10^{4}	$.16935 \times 10^{-4}$
10	hc^2	5.8843×10^{-6}	$.16994 \times 10^{6}$

This series could be expanded, but the functions do not seem to be of importance.

TABLE VIII

		Functions related to c^{12}	Reciprocals
1*	c^{12}	$.52712 \times 10^{126}$	1.8971×10^{-126}
2*	3^{12}	$.53144 \times 10^{6}$	1.8817×10^{-6}
3	$1/6\pi$	$.53052 \times 10^{-1}$	1.8850×10
4	$\dfrac{1}{2\pi c}$	$.53088 \times 10^{-11}$	1.8837×10^{11}
5	ϵ/m_0	$.53035 \times 10^{18}$	1.8855×10^{-18}
6	a	$.53084 \times 10^{-8}$	1.8838×10^{8}
7	$\dfrac{v^2}{c^2}$	$.53051 \times 10^{-4}$	1.8850×10^{4}
8	$\dfrac{\epsilon^2}{h^2}$	$.53086 \times 10^{34}$	1.8837×10^{-34}
9	ϵ/c^2	$.53072 \times 10^{-30}$	1.8842×10^{30}
10	h^2/c^4	$.53061 \times 10^{-94}$	1.8846×10^{94}
11*	$\dfrac{\epsilon}{\pi\sqrt{1846.8G}}$	$.53019 \times 10^{-4}$	1.8861×10^{4}
12	$\dfrac{1}{2\pi\sqrt{m_0}}$	$.53070 \times 10^{13}$	1.8843×10^{-13}
13	$\dfrac{1}{4\pi^2\epsilon}$	$.53103 \times 10^{8}$	1.8831×10^{-8}
14	$\dfrac{1}{3\pi Gc}$	$.53110 \times 10^{-4}$	1.8829×10^{4}
17*	$(3\pi)^4$	$.53000^4 \times 10^{5}$	$1.8868 \times 10^{-5/4}$
23*	$\dfrac{\epsilon}{(2\pi\,1846.8)^2 G}$	$.53161 \times 10^{-9}$	1.8811×10^{9}
35	$\dfrac{\epsilon}{\sqrt{m_0}c}$	$.53054 \times 10^{-6}$	1.8849×10^{6}
36*	$\dfrac{8\pi\,1846.8^3}{3}$	$.52768 \times 10^{11}$	1.8951×10^{-11}

TABLE IX

		Functions related to c^{14}	Reciprocals
1*	c^{14}	4.7377×10^{146}	$.21107 \times 10^{-146}$
2*	3^{14}	4.7830×10^{6}	$.20975 \times 10^{-6}$
4	$\dfrac{c}{2\pi}$	4.7714×10^{9}	$.20958 \times 10^{-9}$
5	$\dfrac{\epsilon c^2}{m_0}$	4.7667×10^{38}	$.20979 \times 10^{-38}$
7	v^2	4.7681×10^{16}	$.20973 \times 10^{-16}$
8	$\dfrac{\epsilon^2 c^2}{h^2}$	4.7706×10^{54}	$.20962 \times 10^{-54}$

TABLE IX (Continued)

		Functions related to c^{14}	Reciprocals
9	ϵ	4.770×10^{-10}	$.20964 \times 10^{10}$
10	$\dfrac{h^2}{c^2}$	4.7690×10^{-74}	$.20969 \times 10^{74}$
11*	$\dfrac{\epsilon c^2}{\pi\sqrt{1846.8G}}$	4.7651×10^{16}	$.20986 \times 10^{-16}$
12	$\dfrac{c^2}{2\pi\sqrt{m_0}}$	4.7698×10^{33}	$.20965 \times 10^{-33}$
13	$\dfrac{c^2}{4\pi^2\epsilon}$	4.7728×10^{12}	$.20952 \times 10^{-12}$
14	$\dfrac{c}{3\pi G}$	4.7734×10^{16}	$.20950 \times 10^{-16}$
23*	$\left(\dfrac{c}{2\pi 1846.8}\right)^{2}\dfrac{\epsilon}{G}$	4.7780×10^{11}	$.20929 \times 10^{-11}$
26*	$\dfrac{1}{\pi G}$	4.7765×10^{6}	$.20936 \times 10^{-6}$
27	$\dfrac{4\pi (1846.8)^2}{c^2}$	4.7685×10^{-14}	$.20971 \times 10^{14}$
28	μa	4.7718×10^{-36}	$.20956 \times 10^{36}$
33*	m_{He}	4.7757×10^{-26}	$.20939 \times 10^{26}$
35	$\dfrac{\epsilon c}{\sqrt{m_0}}$	4.7684×10^{14}	$.20971 \times 10^{-14}$
38	$\dfrac{4\pi(1846.8)^2}{m_0}$	4.7653×10^{34}	$.20985 \times 10^{-34}$
47*	$\beta = h/k$	4.7753×10^{-11}	$.20941 \times 10^{11}$

TABLE X

		Functions related to c^{16}	Reciprocals
1*	c^{16}	42.581×10^{166}	$.023483 \times 10^{-166}$
2*	3^{16}	43.047×10^{6}	$.023231 \times 10^{-6}$
4	$c^3/2\pi$	42.884×10^{29}	$.023319 \times 10^{-29}$
9	ϵc^2	42.872×10^{10}	$.023325 \times 10^{-10}$
10	h^2	42.863×10^{-54}	$.023330 \times 10^{54}$
26*	$\dfrac{c^2}{\pi G}$	42.931×10^{26}	$.023293 \times 10^{-26}$
27	$4\pi 1846.8^2$	42.859×10^{6}	$.023332 \times 10^{-6}$
31*	$\sqrt{1846.8}$	42.974	$.023270$
32	μv^2	42.861×10^{-12}	$.023331 \times 10^{12}$
33*	$m_{He} c^2$	42.923×10^{-6}	$.023300 \times 10^{6}$

TABLE XI

		Functions related to c^{18}	Reciprocals
1*	c^{18}	3.8271×10^{188}	$.26127 \times 10^{-188}$
2*	3^{18}	3.8742×10^{8}	$.25812 \times 10^{-8}$
31*	$\sqrt{1846.8}\ c^{2}$	3.8624×10^{22}	$.25890 \times 10^{-22}$
34*	$\dfrac{1}{\sqrt{G}}$	3.8737×10^{8}	$.25815 \times 10^{-8}$
39	$\pi\ 1846.8\ G$	3.8664×10^{-4}	$.26864 \times 10^{4}$

TABLE XII

		Functions related to c^{32}	Reciprocals
1*	c^{32}	1813.1×10^{332}	$.55150 \times 10^{-335}$
2*	3^{32}	1853.0×10^{12}	$.53966 \times 10^{-15}$
10*	h^{4}	1837.25×10^{-108}	$.54429 \times 10^{105}$
32*	$(\mu v^{2})^{2}$	1837.1×10^{-64}	$.54434 \times 10^{61}$
40	m_{p}/m_{o}	1846.8	$.54148 \times 10^{-3}$
41	$\dfrac{\epsilon}{\sqrt{G}}$	1847.8×10^{-9}	$.54118 \times 10^{6}$

TABLE XIII

		Functions related to c^{34}	Reciprocals
1*	c^{34}	1.6296×10^{356}	$.61360 \times 10^{-356}$
2*	3^{34}	1.6677×10^{16}	$.59962 \times 10^{-16}$
42*	m_{p}	1.6610×10^{-24}	$.60205 \times 10^{24}$
43	$\dfrac{\epsilon}{\sqrt{1846.8}\ G}$	1.6656×10^{-4}	$.60038 \times 10^{4}$
44	$\sqrt{\dfrac{1846.8}{G}}$	1.6647×10^{5}	$.60072 \times 10^{-5}$

TABLE XIV

		Functions related to c^{36}	Reciprocals
1*	c^{36}	$.14646 \times 10^{378}$	6.8278×10^{-378}
2	3^{36}	$.15009 \times 10^{18}$	6.6625×10^{-18}
34	$\dfrac{1}{G}$	$.15006 \times 10^{8}$	6.664×10^{-8}
42*	$m_{p}\ c^{2}$	$.14929 \times 10^{-2}$	6.6985×10^{2}
45	$3/2$	$.15000$	6.6667

TABLE XV

Relations of Physical Constants to Velocity of Light

1	2	3	4	5	6	7	8
3	3	c	2.99796×10^{10}	$2\pi\epsilon$	2.997×10^{-9}	c	2.998×10^{10}
3^2	9×10^3	m_o	8.994×10^{-28}	$\pi\sqrt{1846.8G}$	8.997×10^{-6}	c^2	8.988×10^{20}
3^4	81×10^3	$m_o c^2$	80.84×10^{-8}	Series not important		c^4	80.78×10^{40}
3^6	$.729 \times 10^3$	$1/k$	$.7294 \times 10^{16}$	ϵ/h	$.7286 \times 10^{17}$	c^6	$.7260 \times 10^{63}$
3^8	6.561×10^3	h	6.547×10^{-27}	ω	6.547×10^{15}	c^8	6.525×10^{83}
3^{10}	5.905×10^4	hc^2	5.884×10^{-6}	Series not important		c^{10}	5.865×10^{104}
3^{12}	$.5314 \times 10^6$	ϵ/m_o	$.5303 \times 10^{18}$	v^2/c^2	$.5305 \times 10^{-4}$	c^{12}	$.5271 \times 10^{126}$
3^{14}	4.783×10^6	ϵ	4.770×10^{-10}	m_{He}	4.776×10^{-26}	c^{14}	4.738×10^{146}
3^{16}	43.05×10^6	$m_{He}c^2$	42.92×10^6	μv^2	42.86×10^{-12}	c^{16}	42.58×10^{166}
3^{18}	3.874×10^8	$1/\sqrt{G}$	3.874×10^3	$\pi 1846.8G$	3.866×10^{-4}	c^{18}	3.827×10^{188}
3^{22}	3.138×10^{10}	π	3.1416			c^{22}	3.092×10^{230}
3^{32}	1853.0×10^{12}	m_p/m_o	1846.8	$\epsilon/\sqrt{G}$	1847.8×10^{-9}	c^{32}	1813.1×10^{332}
3^{34}	1.668×10^{16}	m_p	1.661×10^{-24}			c^{34}	1.630×10^{356}
3^{36}	1.501×10^{18}	$1/G$	1.501×10^8			c^{36}	$.1465 \times 10^{378}$

In these tables closely related functions are given the same number. In each table one of these numbers is italicized and all functions different numerically from the value of this italicized function by more than one part in a thousand are marked with an asterisk above the number.

Again ignoring the decimal point (see section 6) it will be at once evident that the agreement shown between the figures given in each table could only occasionally be accidental. It was finally found that all of the different series of figures are related one to another and that apparently all were related to the velocity of light. This relationship is brought out clearly in Table XV. In columns 1 and 2 are shown even powers of 3 to 3^{36}. Similarly in columns 7 and 8 are shown even powers of the velocity of light to c^{36}. Ignoring the decimal point the velocity of light differs from 3 by about one part in fifteen hundred. Nevertheless when both have been raised to the thirty-sixth power the divergence is increased to more than two per cent. The basic constants and a few derived constants are shown in columns 3, 4, 5, and 6. All of these constants (except π) and all of the derived functions shown, and nearly all in the extensive series of functions of which they serve only as examples, lie in value between the respective powers of 3 and c.

This result is amazing.

It follows at once that all other similar functions involving these basic constants will similarly be related numerically through the velocity of light.

One may ask "How can light cause the mass of the electron, the electronic charge, Planck's constant and other constants to have their present values?" A little reflection will show that one has an equal right to turn this question backwards and ask "How is it that the mass of the electron, the electronic charge, Planck's constant and other constants, cause light to have its present velocity?" Still further reflection will show that *Table XV really indicates simply a numerical relationship between these basic constants and light and that a similar table could be constructed using any one of the constants as a basis.* From this standpoint there is nothing necessarily unique about the velocity of light. The importance of Table XV as it stands lies in the fact that it reveals a hitherto unknown numerical relationship between the fundamental constants shown.

It becomes important therefore to study this numerical relationship in detail.

1. Could the Relationship shown be Accidental?

When the first few numerical agreements between the gravitational constant and other constants were noted when dealing with functions, which were not known to be related and which differed in their assigned dimensions, the author was skeptical as to the valuable character of such agreement. As the number of similar functions increased, common sense and experience with calculations were sufficient to enable one to conclude with certainty that the relations were not merely accidental coincidences. Now it is quite possible to state the relations in such form that anyone who desires can apply the laws of probability.

Ten numerical functions are involved as follows:

$$2, 3, \pi, c, m_o \text{ or } \mu, k, h, \epsilon, m_p, G.$$

The mass loss in the formation of helium is omitted from the list as no one is certain of the derivation of the cosmic rays. It may be granted, for the present, that the similarity between 3 and 2.99796 is accidental. Moreover G. N. Lewis has shown that h can be calculated from function 30 of Table VI. This reduces the supposedly unconnected numerical constants to eight.

Moreover G. N. Lewis has recognized the fact that ordinary equations connecting some of the remaining constants can be used to derive what he calls ultimate rational units, and has stated that properly defined units will produce always simple numbers. He has made further use of this fact to calculate h, the constant of Stefan's law and a constant in the equation for the entropy of monatomic[1] gases. His reasoning has been rather vigorously disputed.[2] Bridgman states that Planck was the first to suggest a system of ultimate rational units.

These articles do show that extensive numerical simplification would result from changing our system of units. But the articles do not prove the complete numerical simplicity that exists in our present system (see Table XVII) nor show the connection between this simplicity and the velocity of light. Nor do they prove numerically simple relations between the masses of the proton and electron and gravitation. Moreover the views, as advanced, have not been sufficiently proved to lead to a general recognition of their validity.

Now one might assume roughly that each constant is measured to an accuracy of one part in one thousand. In calculating any given function from a combination of these constants, if there is no actual relation between the constants, a new numerical series should be introduced not only with each combination of constants but with every variation in the power of any constant.

An inspection of the functions calculated will show that the constants are used in some of the various functions to the variation in the powers shown below:

Functions	2	π	c	m_o or μ	k	h	ϵ	m_p	G
Variation in power used	4	5	4	4	1	3	5	5	3

Both the laws of probability and the theories of numbers will show that combinations of unrelated constants as made could produce agreeing numerals only rarely. (Functions that contain 3 as a factor may be based on wholly accidental agreement). Any explanation of the numerical agreement shown as being a mere series of coincidences is utterly impossible. Still more impos-

[1] G. N. Lewis and E. Q. Adams: Phys. Rev., (2) 3, 92 (1914); G. N. Lewis: Phil. Mag. 45, 266 (1923); 49, 739 (1925); G. N. Lewis, G. E. Gibson and W. M. Latimer: J. Am. Chem. Soc., 44, 1008 (1922).

[2] Norman Campbell: Phil. Mag., 47, 159 (1924); O. J. Lodge: 45, 276 (1923); 49, 751 (1925).

sible would it be for the various series of numbers showing such agreement to be accidentally related to each other and to the velocity of light in the manner shown.

The numerical agreements shown must be recognized as a basic fact connecting physical constants.

Yet two more facts must be recognized as having a direct bearing upon any possible accidental numerical agreement among the various functions.

a) Strange as it may seem from the character of the functions calculated, very few of these functions were originally calculated for the purpose of showing numerical agreement. Almost all of the forty-seven functions, shown in Table XVIII, to which the others can be immediately reduced, were either previously recognized as being of "natural" significance, or were calculated by the author in the progress of certain theoretical investigations.

b) As shown under Section 5, headed "Can Exact Numerical Agreement be obtained?" only slight changes are necessary in the values of the constants at present adopted to make nearly all of the functions shown in any given series give numbers agreeing to one part in five thousand. With very many functions there would be perfect agreement.

2. The Exactness of the Agreement

Of all of the results shown in Tables II-XIV only the following differ from the underscored function number in each table by more than one part in five hundred (ignoring the decimal point).

Powers of c and 3. c and 3 differ as to the numerals involved by only about one part in 1500. Nevertheless when the numbers are raised to high powers, a serious multiplication of this difference is of course evident.

Functions 37 Table II, 15 Table IV, 16 Tables III and IV, 36 Table VIII, and 31 Table X, all contain 1846.8 as a factor. As is well known, calculations based on spectroscopic evidence lead to the value of this ratio as about 1838. Calculations based on deflection measurements lead to the value 1846.8. Apparently some such divergence is at the bottom of the disagreement shown by these functions. The recent discovery of an isotope of hydrogen must also be considered.

Functions 10 and 32 of Table XII give 1837.25 and 1837.1 as numerals, confirming evidence based on spectroscopic determinations. Function 42 of Table XIV is the only function included in the tables differing from the expected numeral by more than one part in 500 for whose divergence we can at present find no reason.

A few other additional functions as shown by an asterisk differ from the underscored function by as much as one part in a thousand. These differences usually do not probably arise entirely from the uncertainty of the basic constants used. They arise from the fact that 3, m_o, and μ are probably not always correctly used and from the further fact that certain existing disturbances (as for instance a disturbance caused by the physical dimensions of the particle) should be allowed for and were not. It seemed best to the

author not to attempt to apply minor corrections to any function, since such an attempt might lead to the feeling that the agreements had been obtained by unjustifiable modifications.

3. The Dimensions of the Functions compared

The author has already been accused even before the publication of this paper of paying no heed to the dimensions of the functions compared. This may indeed be a grievous error. But if it is, the author is not to blame. The mistake was made by nature. All the author has done is to show that a numerical relation actually exists between quantities of different dimensions. Nature, not the author, must be called on to explain why.

The author indeed has no intention of engaging in the oft repeated discussion of dimensions. It is commonly granted that magnetic permeability and the dielectric constant are mutually related to the velocity of light. That discovery marked a big step forward and leaves us with only three dimensions concerning which to worry—mass, length, and time, since temperature is known to be related to kinetic energy. The relativity theory has insisted upon a connection between length and time and the velocity of light is concerned also with that relation. The implied connection found by the author is of a very different character, but again concerns the velocity of light and at any rate the imagination is not further strained. This leaves only mass to worry about. No one knows what causes mass, but it is a step forward to find that mass also is connected with light and time, and again through the velocity of light. Others have advanced ideas concerning the possible electromagnetic nature of mass. Such theories presuppose the possibility of omitting mass as an ultimate dimension.

The idea of dimensions can be made to serve a very useful purpose, but there is often times confusion in their use. One is quite accustomed to the idea that mv represents the momentum of a moving particle and $1/2\,mv^2$ its kinetic energy. But the fact that we have chosen to square the velocity of the particle, and give the name energy to the function thus obtained, has not changed the actual velocity of the particle one iota. The particle still has the same velocity and the dimensions attributable to the particle are still ml/t. We have merely chosen to take two other dimensions l/t, which really belonged to the space traversed by the particle, and have attributed these dimensions also to the particle. This is mathematically very convenient, but it should not be allowed to obscure the fact that energy is in reality a function of the space traversed as well as of the particle, and is dependent on both.

So mass should be regarded as a dimension of a particle only until we realize the true nature of the ultimate property which is its cause. Personally the author believes ultimately that mass will be found to be a property of the physical dimensions of the particle concerned and of the energy of the surrounding space. In other words, it is a property concerned with the distribution of energy in space.

4. The Relationship between 2, 3, π, and c

At first one of the most baffling phases of the numerical relations found to exist was the fact that ignoring the decimal point the following relations were very approximately true:—

<div align="center">

TABLE XVI

Relations between 2, 3, π and c

</div>

		Corresponding Value of c			Corresponding Value of c
2	$= 1/c^{35}$	3.00005	3π	$= c^{23}$	3.00015
3	$= c$	3.00000	4π	$= 1/c^{48}$	2.99985
3/2	$= c^{36}$	2.99995	6π	$= 1/c^{12}$	2.999565
π	$= c^{22}$	3.00019	$3/2\pi$	$= c^{14}$	2.99963
2π	$= 1/c^{18}$	2.999601			

All of the functions can be derived from those for 2π, 4π and 6π, or from any three of the functions that contain the factors 2, 3 and π. The equations do not necessarily exist simultaneously in nature with regard to the same functions and the author thought that a careful determination of the corresponding value of c might lead to the rejection of some one of the relations. But the greatest divergence of any of the values of c from the mean value is as shown in Table XVI, only one part in 10,000. Another surprising result of this check is that all values of c are considerably above the actual observed value. For a discussion of this point see under Section 5.

Actually in nature the relationship probably arises from such equations as

$$1/2\pi c = \text{a function which reduces numerically to } c^{12}, \text{ or}$$

$$4\pi\,(1846.8)^2 = \text{a function which reduces numerically to } c^{16}$$

and from the possible accidental relation numerically of 3 to 2.99796. If the natural relations concerned could be determined all of the others could be discarded as of no consequence in spite of their very close similarity numerically to other naturally arising functions. Curiously enough the first Bohr orbit of the electron and proton is almost exactly 1000/c and the orbit which would correspond with a loss of energy equivalent to Millikan's longest cosmic ray is 1/1000c. The corresponding radii of the orbits are 1000/2πc and 1/2000πc. Other unique points in nature give rise to similar simple relations and serve to make clear that such relations concerning π as those shown above will exist. Why the orbits are at the points stated is a much more baffling problem.

No reason is known why $8\sqrt[3]{\pi^5}/15$ should be related to c^7,[*] nor why 3π should be related to $c^{12} \times 10^{-5/4}$.

5. Can Exact Numerical Agreement be obtained?

The best way to answer this question is to choose a single function and calculate all values and constants from this function. For this purpose, we

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[*] See G. N. Lewis and E. Q. Adams: Phys. Rev. (2) **3**, p. 92 (1914).

choose the function $2\pi c = 1/c^{12}$. The choice of the function may be regarded for the present as somewhat arbitrary although it was selected because the radius of the first Bohr orbit as stated above is $1000/2\pi c$. The results of the calculation are given in Table XVII.

TABLE XVII

Calculation of Physical Constants from the Equation $1/2\pi c = c^{12}$

		Observed			Calculated
c	c	$(2.99796$	$\pm 0.00004)$	$\times 10^{10}$	2.99960
c^2	m_0	$(8.994$	$\pm 0.014)$	$\times 10^{-28}$	8.99761
c^6	$1/k$	$(7.294$	$\pm 0.0074)$	$\times 10^{15}$	7.28415
c^8	h	$(6.547$	$\pm 0.008)$	$\times 10^{-27}$	6.55402
c^{14}	ϵ	$(4.770$	$\pm 0.005)$	$\times 10^{-10}$	4.77401
c^{34}	m_p	$(1.6610$	$\pm 0.0017)$	$\times 10^{-24}$	1.66014
c^{36}	$1/G$	$(1.5006$	$\pm 0.0005)$	$\times 10^{7}$	1.49373

The decimal points have again been ignored in making this calculation (See Section 6).

The divergence of $1/k$ is probably due to the size of the molecules of the gas. This point will be considered in a later paper.

As regards the velocity of light it should be borne in mind that if an ether does exist made up of discrete particles, and if a mechanical explanation of the universe is possible, then the velocity of light will differ from the velocity of the particles that cause the wave.

Table XVII at the present time should be taken only as an indication of the possible aid that may be obtained from the relations shown in determining more accurately the value of physical constants. The author regards the constants as calculated at the present time as possible "ideal" constants that would be produced if the ether particles were reduced to points which retained their present properties.

Use can be made of the facts brought out by the table to bring into prominence certain simple relations which should aid in arriving at the underlying cause of the relations shown. Thus it is useful to recognize that using the calculated constants $Gm_0m_p = 10^{-58}$ exactly, and that numerous similar exact relations will hold.

The facts given may furnish a clue to the cause of the present discrepancy between certain spectroscopic and deflection measurements.

There are numerous other possibilities suggested. The author was led by a simple speculation in connection with the facts to the discovery that the mass loss causing Millikan's longest cosmic rays is numerically 7.294 times Planck's constant and Planck's constant is of course numerically 7.279 times the mass of the electron. One may indeed be allowed to guess that perhaps the mass loss represented by these rays is more accurately 7.284 times Planck's constant, and that the mass loss represented by the shortest cosmic rays is 7.284 times the mass loss represented by the longest rays.

The first Bohr orbit of the electron and proton is $1000/c$ in length and the orbit under the same law required for Millikan's longest cosmic rays is $1/1000c$. Is it possible that these cosmic rays have their origin in the formation of the proton itself? Is it possible that the proton is produced by two electrons moving in an orbit with semi major axis 1.526×10^{-16} centimeters? Is it possible for an electron to move in an orbit which would normally give to the electron a velocity above the velocity of light? Does the motion of an electron in such an orbit give rise to a positive charge and a large increase in mass? Is the electron an ether particle which has "lost" some of its velocity? At the present time these are mere speculations caused by an attempt to follow back ideas suggested by the relations shown. They are cited here only to show that the facts followed back suggest possibilities from which perhaps the false may be sifted.

6. The Decimal Point

In calling attention to the numerical relationships the decimal point has been ignored. In considering the entire function the decimal point cannot be ignored. As explained, Table XV is artificial in that it appears to make all of the constants depend numerically on the velocity of light. What the table really indicates is a numerical relation among the various constants shown and any constant shown could be made the basis for the table. The correct ultimate table would probably (from the author's point of view) be based in part on more fundamental constants. Between certain constants reciprocal relations exist and one or more physical entities which partly give rise to a property are eliminated. Thus time does not appear directly in Table XV nor does the volume of the masses.

The constants really concerned in the relations appear to be 2, 3, π and c. Using some of these numbers above it is quite possible to write such functions as $h = \dfrac{3^{11}}{c^3}$, $m_p = \dfrac{3^{38}}{c^4}$, $\dfrac{1}{G} = \dfrac{3^{37}}{c}$, where the 3 is more exactly 2.9996. Numerous similar relations could be written all of no value unless the true relations existing in nature were found. Introducing some theoretical considerations the author suspects strongly that 2, 3, π, and c will all be concerned in the equations which really represent nature. Thus G appears numerically to be related to c^{36}. In reality the relations $G = 2000/c$ and $1/\pi G = 4.7765 \times 10^6$ are probably a somewhat nearer approach to nature, nor is the possible introduction of a logarithmic relation absurd, either theoretically or numerically.

It should be realized that the ratio of the functions in any one of the Tables II–XIV will give a power of 10 very nearly, and that if the calculated constants shown in Table XVII are used then the ratio will often be an exact power of 10. When this fact is considered and it is further realized that we must go one step back of our present physical constants in representing nature in the simplest manner then the fact that we have ignored the decimal point in deriving the relations existing with our present units should not cause any feeling of skepticism. There is nothing mystical concerning the relations.

7. Summary of Functions calculated

A summary of the more important functions calculated are shown in Table XVIII. It appears somewhat strange that the natural functions seldom lead to simple numerical relations involving odd powers of c, though of course a few such functions have assumed some importance.

TABLE XVIII
Summary of Functions

No	Function	Value	No	Function	Value
1	c	2.99796×10^{10}	36	$\dfrac{8\pi 1846.8^3}{3}$	52.768×10^9
2	3	3.00000	35	$\dfrac{\epsilon}{\sqrt{m_0 c}}$	53.054×10^{-8}
13	$2\pi\epsilon$	2.9971×10^{-9}	17	3π	$53.000 \times 10^{5/4}$
14	$\dfrac{3Gc}{2}$	2.9967×10^3	9	ϵ	4.770×10^{-10}
37	$\dfrac{I}{2 \times 1846.8 m_0}$	3.0102×10^{23}	33	m_{He}	4.7757×10^{-26}
12	m_0	8.994×10^{-28}	26	$1/\pi G$	4.7765×10^6
25	$\pi\sqrt{1846.8}\,G$	8.9969×10^{-6}	7	v^2	4.7681×10^{16}
24	$\dfrac{\epsilon^3}{1846.8h}$	8.9762×10^{-6}	4	$c/2\pi$	4.7714×10^9
15	$\dfrac{\sqrt{1846.8}}{\epsilon}$	9.0093×10^{10}	I	$3/2\pi$	4.7746×10^{-1}
16	$\dfrac{I}{1846.8G}$	8.1255×10^8	47	$\beta = h/k$	4.7753×10^{-11}
46	$\dfrac{\sqrt{1846.8}\,m_0}{\epsilon}$	8.1024×10^{17}	28	$\mu a = m_0 a_0 = m_p a_p$	4.7718×10^{-36}
21	h/m_0	7.279	38	$\dfrac{4\pi(1846.8)^2}{m_0}$	4.7653×10^{34}
20	m_{He}/h	7.294	27	$4\pi 1846.8^2$	42.859×10^6
8	ϵ/h	7.2860×10^{16}	32	μv^2	42.861×10^{-12}
19	$\tau = I/k$	7.2886×10^{15}	31	$\sqrt{1846.8}$	42.9744
18	$3/2\pi h$	7.293×10^{25}	39	$\pi 1846.8 G$	3.8664×10^{-4}
22	$\dfrac{(2\pi\epsilon^2)^2}{h^3}\dfrac{v^2}{h}$	7.283×10^{42}	40	$\dfrac{m_p}{m_0}$	1846.8
10	h	6.547×10^{-27}	41	$\epsilon/\sqrt{G}$	1847.8×10^{-9}
29	$\omega = 2R_H c$	6.5467×10^{15}	42	m_p	1.6610×10^{-24}
30	$\dfrac{(4\pi\epsilon)^2}{c}\sqrt[3]{\dfrac{8\pi^5}{15}}$	6.5497×10^{-27}	43	$\dfrac{\epsilon}{\sqrt{1846.8G}}$	1.6656×10^{-4}
3	$1/6\pi$	53.052×10^{-8}	44	$\sqrt{\dfrac{1846.8}{G}}$	1.6647×10^5
5	ϵ/m_0	53.035×10^{16}	34	$1/G$	$.15006 \times 10^8$
6	a	53.084×10^{-10}	45	$3/2$	$.15000$
4	$1/2\pi c$	53.088×10^{-13}			
14	$1/3\pi Gc$	53.110×10^{-6}			
11	$\dfrac{\epsilon}{\pi\sqrt{1846.8G}}$	53.019×10^{-6}			
23	$\dfrac{\epsilon}{(2\pi\,1846.8)^2 G}$	53.161×10^{-11}			

The functions shown in Table XVIII are all dependent upon the relations already discussed between the more fundamental constants 2, 3, π, c, m_0, k, h, ϵ, m_p, and G. The derived functions give however sometimes an unexpected hint as to the nature of the relations between the fundamental constants. Actually a study of the derived functions led to the finding of the numerical relationship between the fundamental constants. Their further study may suggest the complete relationship.

8. Some Suggestions as to the Ultimate Meaning of the Facts

The author does not believe that there is anything in the facts brought out which justifies representing mass or time as a length, or which requires very radical readjustment of primary ideas. A simple numerical relation has been found to exist between fundamental physical constants and these simple relations would be extended by new definitions of atomic weights and certain other constants. But the physical realities existing remain as before.

On the other hand the simple numerical relations proved to exist indicate actual relations between the physical entities concerned of a nature not yet fully realized. For example no simple numerical relation will exist between the mass of an atom of tin or lead and the velocity of light. If therefore a simple relation is found between the mass of the proton and the mass of the electron and the velocity of light a fact has been discovered which requires some sort of an explanation. For there is no *a priori* reason why the complexity of the proton and electron might not prohibit any simple numerical relation between them and between other physical constants.

The author believes that the facts shown are of such a nature as to point rather strongly to the idea that a mechanical explanation of the universe is possible. Certain particles (masses) existed in the universe. A certain amount of motion (energy) was available, and finally distributed itself among the existing particles. As a result we finally have "created" the masses of proton and electron, electronic charge, Planck's constant, the velocity of light, gravitation, and the various attractive forces and results dependent upon them. Protons and electrons apparently exist in equal numbers and the suspicion that both are "created" from some possible simpler particle, such as an ether particle, is increased by the numerical relationships discovered.

Following out the ideas above in a little more detail it seems to the author probable that an ultimate unit of time is desirable and probably would be best defined as the time required for an ether particle to traverse the space which it occupies due to its motion. This is in order to prevent undue multiplication of the space occupied by the particle in relations concerning its motion. Then if it be assumed that this fundamental space traversed in a unit of time bears a simple relation to the orbit which defines the proton and that the diameters of the particles themselves are not greater than 1/12 of the diameter of this orbit, the simple numerical relations shown might possibly follow.

Summary

1.   Simple numerical relations have been shown to exist between the constants π, m_o, $1/k$, h, ϵ, m_p, and $1/G$, and the velocity of light, and therefore such relations exist between all functions calculated from them.

2.   The fact that such a relation exists proves a connection between the constants not as yet understood.

3.   The above constants can be calculated from the equation $1/2\pi c = c^{12}$ and their relation to certain powers of the velocity of light, if the decimal point is ignored.   This indicates that the relation which exists is of a very simple nature.

University of South Carolina,
Columbia, S. C.
January 21, 1932.

THE INFLUENCE OF ELECTROLYTES ON THE SPECIFIC HEAT OF WATER*

BY FRANK URBAN

The Hofmeister series or lyotropic series[1,2,3,4] was discovered by Hofmeister. It deals with the effects of neutral salts on the protein colloids. The anion series is F^-, ClO_3^-, CO_3^{--}, SO_4^{--}, tartrate, citrate, acetate, Cl^-, Br^-, NO_3^-, I^-, CNS^-; the cation series Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Li^+, Na^+, K^+, $(NH_4)^+$, Rb^+, Cs^+. It is in this order that these ions influence the swelling, osmotic pressure and viscosity of protein colloids. These ions act in an analogous manner on the temperature of gel formation of a gelatine solution, and on the time of gelation. The ions first in the series have the greatest effect. The temperatures at which swelling of starch occurs, also follows the Hofmeister series. It should be noted that the cation series is less definite and less well established than the anion series.

The series is encountered also outside of the field of protein solutions. Thus, it has been shown that the solubility of difficultly soluble substances, especially of gases, is influenced by the addition of neutral salts, in the order of the Hofmeister series. The series is also encountered in the order of the change of the viscosity of water by salts. The saponification of esters, the surface tension of water, and the electrolytic solution pressure are all influenced by neutral salts in the order of the Hofmeister series. The anomalies in the lowering of the freezing point shown by concentrated solutions differ for different salts; the anions may be arranged to form a Hofmeister series.

Bancroft[5] offered good arguments to prove that these phenomena associated with the Hofmeister series may be due to a change in the solvent (water). He showed that they can not be explained on the basis of specific colloidal effects.

That a shift in the equilibrium between different molecular species can bring about decided changes in the property of a solvent has been demonstrated in the case of alcohol. Bancroft[5] mentions the work of Byron and of Lunge who showed that ether plays no direct part in the peptization of pyroxylin by an alcohol-ether mixture. Ether displaces the equilibrium in the direction of the polymer. The latter is the true peptizing agent. If this is so, then it should be possible to peptize pyroxylin at low temperatures by alcohol alone. Kugelmass, McBain, and Byron found that pyroxylin is peptized by alcohol at low temperatures.

[1] Hofmeister: Archiv exp. Pathol., **25**, 13 (1888); **28**, 210 (1891).
[2] Spiro: Hofmeister's Beitr., **5**, 276 (1904).
[3] Odén and Anderson: J. Phys. Chem., **25**, 311 (1921).
[4] Hoeber: Physik. Chemie der Zelle, **1**, 267 (1922).
[5] Bancroft: J. Phys. Chem., **30**, 1194 (1926).

It seemed promising therefore to study the water equilibrium in connection with these questions. A thermodynamic method was chosen for this purpose. We felt that a determination of the specific heats of solutions, containing the anions and cations of the Hofmeister series, from which the partial molal heats of solvent and solute and their temperature coefficients can be calculated would lead to interesting conclusions. It was reasoned that the abnormally high specific heat of water is occasioned by the presence of polymerized molecules which are broken down, as the temperature is raised, into simpler molecules with the absorption of heat. If the presence of ions of the Hofmeister series causes some of these larger molecules to depolymerize then there should be fewer of the large molecules available for absorbing heat and the heat capacity of water in the solution should be less than the heat capacity of pure water.

The object of this particular investigation was not to obtain the greatest possible precision in the measurement of aqueous solutions of electrolytes but rather to cover a considerable range of temperature and concentration with salts which are significant in the Hofmeister series. Dilute solutions, which are particularly significant for theories of ionization, were not investigated but emphasis was placed on concentrated solutions because in them the change in the solvent is most pronounced. The solvent rather than the solute was the center of interest.

Apparatus

For the investigation, an adiabatic calorimeter was used. It is obvious that the heat leakage can be reduced almost to zero, if the system can be made perfectly adiabatic. This result can be achieved by electrolytic heating[6] of the outer bath and by our automatic adiabatic control.

The apparatus used in the determinations of specific heats is shown diagrammatically in Fig. 1. It was a modified form of the apparatus of Williams and Daniels,[7] in which temperatures are measured with a platinum resistance thermometer set in the *outer* bath so as to eliminate thermal leakage along the thermometer to the calorimeter. The readings are taken only when the calorimeter and the outer bath have identically the same temperature as indicated by a zero reading on a thermocouple. The solution was contained in a cylindrical solid silver cup 1, having a capacity of about 0.6 liter supported in an enclosing vessel with an air gap O of 9 mm. between the two. It rested on three Bakelite points. The enclosing vessel 2 was of copper, fitted with a threaded cover of bronze. The cover was provided with an upright tube for the stirrer N, and conical stuffing boxes for the admission of the heater H, and thermocouple C. The heater leads ran through the bath for about 20 cm. to prevent thermal leakage to the air of the laboratory. The cover, with all of the parts supported by it, was screwed into a ring brazed to the copper cylinder. A mixture of oil and graphite in the threads kept the joints tight and acted as a lubricant.

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[6] Daniels: J. Am. Chem. Soc., **38**, 1473 (1916).

[7] Williams and Daniels: J. Am. Chem. Soc., **46**, 903 (1924).

The inner stirrer shaft N was made of Bakelite and carried two silver propellers. The Bakelite shaft was screwed to a brass shaft. This upper shaft rotated on two ball bearings. A cap Q attached to it, rotated in the liquid of the outer bath, thus forming a seal and preventing the movement of air, and reducing losses by evaporation to a minimum.

The stirring was found to be most satisfactory at about 130 R.P.M. At this speed, the stirring of the solution was quite efficient and the heat of stirring was of the order of 0.001°C per minute. The exact value was obtained for each determination.
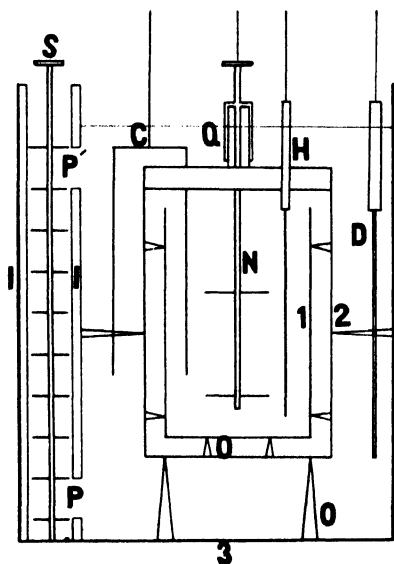
Fig. 1
Calorimeter

A thermel, C, of 16 copper-constantan thermocouples was enclosed in a thin glass tube, and connected to a Leeds and Northrup H. S. galvanometer having a sensitivity of 10 mm. per microvolt at 1 m. The scale was placed at a distance of 4.5 meters from the galvanometer and each cm. of the scale corresponded to a temperature difference of 0.0006°. The resistance of the thermel was 40 ohms. The enclosing tube was filled with a light mineral oil to reduce the thermal lag. At lower temperatures ice water was circulated through a cooling jacket I in the outer bath. Thorough stirring of the outer bath was obtained by means of a stirrer, rotating at about 1800 R.P.M. in the cylindrical compartment S, which sucked the water in at P and emitted it at P'. At temperatures above room temperature, when the outer bath had a tendency to cool off, an adjustable reactance in series with an electric heating coil kept the outer bath nearly up to the temperature of the experiment. This reactance could be set to deliver energy just sufficient to compensate for heat losses by evaporation and cooling.

A Leeds and Northrup calorimetric, platinum-resistance thermometer D, in the outer bath, indicated the temperature of the outside bath. The temperature in the calorimeter was exactly equal to that indicated by the resistance thermometer in the outer bath when the thermel-galvanometer registered zero. If it did not register exactly zero a small correction, amounting to 0.002° or less was applied. Usually, no correction was necessary.

The platinum thermometer was read on a Leeds and Northrup high precision bridge, in connection with a high-sensitivity galvanometer. It was calibrated at the ice point, the boiling point of water and the transition temperature of sodium sulphate. The sensitivity was such that changes of 0.0005° C could readily be detected.

The Automatic Adiabatic Control

The adiabatic control was made automatic with the help of a selenium cell. Light from a 60-watt automobile head light was projected on the mirror of the galvanometer, connected with the thermel. This light was cooled by a stream of water. The galvanometer mirror reflected this light on a selenium cell which was located at a distance of about 4.6 meters from the galvanometer. The cell had a resistance of about 120,000 ohms, when illuminated; in the dark, its resistance increased to about 200,000 ohms. The cell was in series with a grid leak of 250,000 ohms and three dry cells. The terminals of the grid leak were connected to the grid and filament of a radio tube (Cunningham, Type EX-112), respectively. Any change in the resistance of the selenium cell caused a fluctuation in the space current of the radio tube. The space current was about 2 milli-amp. when the selenium cell was in the dark; and 1 milli-amp. when it was illuminated. The space current flowed through a micro-relay. A counter E.M.F., supplied by a storage battery, was put across the micro-relay. It yielded exactly one milliampere and thus the net effect was a current of one milliampere when the cell was dark, but no current passed when the cell was illuminated. If small fluctuations occurred in the space current, the counter E.M.F. was immediately adjusted by varying the resistance in a 10,000 ohm resistance box, in series with the storage battery. The micro-relay in turn actuated larger relays, which controlled the heating of the outer-bath. When the outer bath was colder than the calorimeter the beam of light was thrown to the left of the selenium cell, the micro-relay was closed and the outer bath was heated by the passage of the current through the water. The outer bath then heated up faster than the calorimeter and threw the beam of light of the thermal galvanometer on the selenium cell. The micro-relay was then released, the heating of the outer bath ceased and the beam swung back to the left, whereupon the operation was repeated. A series of small mirrors arranged as a parabola was placed at the right of the selenium cell to reflect the beam back onto the cell in case it swung past, on account of the time-lag of the selenium cell.

The adiabatic control fluctuated between $\pm 0.0015°$ and $\pm 0.004°$ under average conditions. In order to obtain best results, the conductance of the outer bath had to be properly adjusted, as too high a conductance produced too much heat and caused the beam of light to travel entirely across and beyond the parabolic mirror. In actual operation, the conductance could be satisfactorily maintained by adding distilled water to the outer bath from day to day, as needed, to replace evaporation losses.

Procedure

Before starting a determination, ice water was pumped through the calorimeter jacket I (Fig. 1) and the temperature of the outer bath lowered as much as possible (usually to about 6° or 7°C). In the meantime, the solutions were prepared, by weighing a certain amount of salt and conductance water into a Pyrex flask. This solution was then cooled and poured into the silver can,

The can, together with the surrounding copper vessel and brass lid had been previously weighed. The brass lid was screwed on again at once, to avoid condensation of moisture of the air on the cold silver cup. The cap attached to the upper shaft was closed, temporarily, by two halves of a rubber stopper.

The solution was placed in the outer bath of the calorimeter immediately after weighing. Measured amounts of electrical energy were then passed through the heater H, (Fig. 1) for definite time intervals. The time was measured with a calibrated stop watch which read to 0.1 second. While the input of energy into the inner solution continued, the outer bath automatically maintained itself at the same temperature as the solution. After a definite interval, the input of electrical energy into the inner solution was discontinued and its temperature determined, as outlined above. The reading was not taken immediately, but after a period of from 5 to 10 minutes, so as to insure that the solution had come to complete thermal equilibrium. The length of this period was determined and a corresponding correction, for the heat produced by the stirrer, was applied.

Three different heaters were used in the investigation, having resistances of approximately 31, 34 and 40 ohms. They were all made of Constantan wire No. 32, wound in a bifilar manner on a mica strip. The constantan wire was silver-soldered to copper leads. The primary sheath of all three heaters consisted of thin (0.05 mm) copper foil, which was soldered over the heating element. Thin mica sheets served as insulation. Two of the heaters were heavily silver-plated, the plating being more than 0.12 mm. thick. The third heater was not silver-plated, but coated with Bakelite varnish and baked. In no case were we able to detect contamination of our solutions by copper. The fact that the different heaters showed no difference in the specific heat measurements lent confidence to the results.

The electrical system was similar to that described by Williams and Daniels.[8] Ten storage cells supplied the energy which passed through the heater and a standard resistance. In parallel with the heater, there was a volt-box, having a ratio of 20.078:1. The volt-box and standard resistance and standard cell were calibrated by the Wisconsin Electrical Standards Laboratory. The heater, the multiplier, and the standard resistance were all connected to a sensitive potentiometer. The scale was placed at a distance of six meters from the galvanometer.

Determination of Specific Heats

The procedure and calculations are illustrated in Table I with the details of a single experiment.

In this particular experiment the calorimeter contained 584.86 grams (corrected to vacuum) of a 0.500 molal solution of potassium chloride (0.5 mole KCl per 1000 g. of water). In the first column are given the time intervals in seconds during which the electrical heater was turned on. In the second column are given the time intervals which elapsed between turning off the

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[8] Williams and Daniels: J. Am. Chem. Soc., **46**, 908 (1924).

TABLE I

Details of a Calorimetric Measurement

1 Time Heating Seconds	2 Time After Heating	3 Temperature C.	4 Temperature Increase	5 Resist. Heater Ohms	6 Energy Input Joules	7 Input per deg. Joules
0	—	8.6766	—	—	—	—
1830.5	425	12.3220	3.6024	31.872	8652.1	2401.8
1830.1	744	15.9603	3.5949	31.878	8650.7	2406.4
1830.3	724	19.5926	3.3934	31.887	8654.3	2408.4
1830.0	516	23.2210	3.5959	31.889	8652.5	2406.2
1830.1	440	26.8513	3.6015	31.893	8564.3	2403.0
1829.9	611	30.4776	3.5997	31.897	8653.9	2404.1
1830.1	648	34.1009	3.6019	31.901	8656.5	2403.3
1830.1	820	37.7302	3.6082	31.905	8657.6	2399.4

heating current and the measuring of the temperature. The data of the second column are used only in calculating the stirring correction. The temperatures are given in column 3. One of these includes a correction of 0.0015° and another a correction of 0.0022° because the differential thermel was not exactly at zero when the resistance thermometer was read. The others involved no correction. Column 4 gives the actual temperature increase produced by the electrical heating—i.e. the intervals between the figures of column 4 from which has been subtracted the temperature rise due to stirring. This correction due to the heat of stirring was determined over a considerable period of time at the end of each experiment (40°C). Experiments showed that the change in the heat of stirring with the temperature was small enough to neglect.

The current through the system was 0.51066 ampere as measured with the potentiometer across a standard 1 ohm resistance. It was kept constant at all times by raising or lowering a resistance wire in a tube of mercury, placed in series with the heater. The voltage used for measuring the potential drop across the heater drew a small amount of current, 0.01527 ampere, which was subtracted from the total current giving a current of 0.49539 ampere through the heating coil.

The resistances of the heating unit, given in column 5, were obtained by dividing the potential drop across the heater by the current flowing through the heater. The total input of electrical energy in the heater was calculated by multiplying the square of the current through the heater by the resistance and by the time. These values expressed in joules are given in column 6. Division of these values by the temperature interval gives the average number of joules required to raise the calorimeter and the solution through 1°C.

The water equivalent of the calorimeter was determined by similar measurements using pure water, and a curve giving the water equivalent at each temperature was prepared. For the first interval (8.6 to 12.2) it had a value of 78.1 joules per degree. Since 2401.8 joules of heat was required to raise the calorimeter and its contents through 1° in this temperature range, 2323.7

joules was required to raise the contents (584.86 grams of 0.500 molal potassium chloride) through 1°. The heat required to raise one gram of the solution through 1° in this interval is then 3.973 joules or 0.9494 $cal_{15°}$[9].

It is evident that the specific heats calculated in this way are average specific heats covering the temperature interval for which they were determined. This interval varied between 3.5° and 4.5° in the different determinations.

Summary of Results

The average specific heats ($calories_{15°}$ per degree per gram of solution), calculated in the manner just described, were plotted against temperature on a large scale and the interpolated values are summarized in Table II.

TABLE II

Salt	m*	10°	15°	20°	25°	30°	35°	40°
KCl	2.000	.8423	.8431	.8439	.8448	.8457	.8466	.8474
KCl	1.000	.9144	.9123	.9131	.9140	.9148	.9157	(.9166)
KCl	0.500	.9512	.9519	.9526	.9532	.9539	.9547	.9555
KCl	0.100	.9868	.9865	.9862	.9859	.9856	.9853	.9850
BaCl₂	1.384	.7332	.7366	.7378	.7389	.7430	.7470	.7482
BaCl₂	1.000	.7784	.7875	.7892	.7900	.7906	.7914	.7922
BaCl₂	0.500	.8758	.8782	.8798	.8814	.8832	.8848	.8856
BaCl₂	0.100	.9615	.9623	.9623	.9620	.9614	.9610	.9606
KCNS	2.625	.8078	.8120	.8146	.8160	.8162	.8156	.8142
KCNS	1.257	.8908[a]	.8935	.8950	.8958	.8963	.8963	.8963
KCNS	0.500	.9501	.9517	.9524	.9530	.9534	.9537	.9537
K tartrate	2.000	.7568[b]	.7611	.7630	.7639	.7648	.7658	.7667
K tartrate	1.000	.8388[a]	.8462	.8473	.8484	.8496	.8507	.8518
K tartrate	0.500	.9104[d]	.9116	.9139	.9147	.9155	.9164	.9172
K tartrate	0.100	.9553	.9587	.9597	.9607	.9617	.9627	—
KC₂H₃O₂	2.360	.8440[a]	.8479	.8515	.8530	.8530	.8526	.8520
KC₂H₃O₂	0.974	.9202	.9240	.9266	.9271	.9270	.9266	.9259
KC₂H₃O₂	0.479	.9528	.9553	.9561	.9560	.9555	.9548	.9542
KC₂H₃O₂	0.249	.9816	.9843	.9849	.9845	.9835	.9824	.9813
KBr	2.000	.7787[c]	.7795	.7856	.7853	.7855	.7880	.7888
NH₄Cl	2.000	—	—	.8904	.8915	.8925	.8936	.8946

a = 11°; b = 12°; c = 13°; d = 14° instead of 10°.

* Mols per 1000 grams of water.

[9] The conversion factor 4.185 given by Int. Crit. Tables is used in this research.

It is probable that the uncertainty in the data presented in this investigation was usually within 1 or 2 parts per thousand. The errors in the standard resistance, standard cell, volt-box calibration and measurement of time were probably less than 0.02 per cent in each case. The adiabatic control was so perfect that the thermal leakage may be considered entirely negligible. The error due to evaporation of the water, which saturates the air gap in the calorimeter as the temperature is raised, was also negligible. Assuming complete saturation a calculation showed that the evaporation amounted to 0.008 cal. per degree at 7° and 0.04 cal. per degree at 40°. The greatest source of error was involved in the correction for the heat of stirring. Assuming an error of 10 per cent in this quantity the uncertainty in the final result would be 0.1 per cent since the heat of stirring was about 1 per cent of the total heating effect. This error could be reduced with better design and with greater constancy in the rate of stirring.

Partial Molal Heat Capacities

The partial molal heat capacities of potassium chloride $\overline{C}_{p_2}$ were calculated by plotting the apparent molal heat capacity, Φ, against the logarithm of the molality,[10] dividing the slope of the tangent by 2.303 and adding the ordinate. $\overline{C}_{p_2}$ having been found, we obtain $\overline{C}_{p_1}$ (the partial molal heat capacity of the water) by substituting in the equation

$$C_p = n_1 \overline{C}_{p_1} + n_2 \overline{C}_{p_2}.$$

The partial specific heats of the solvent in 0.1 m, 0.5 m, 1.0 m and 2.0 m KCl solutions are shown in Table III.

TABLE III

Partial Specific Heats of Water in Solutions of Potassium Chloride

$\overline{C}_{p_1}$	10°C	15°	20°	25°	30°	35°	40°
0.1 m KCl	.9970	.9965	.9965				
0.5 m KCl	.9948	.9948	.9954	.9952	.9955	.9960	.9971
1.0 m KCl	.9928	.9934	.9940	.9950	.9952	.9961	.9973
2.0 m KCl	.9863	.9899	.9916	.9920	.9929	.9948	.9968

These values have been plotted in Fig. 2. The 25°C value of 0.1 m KCl (Curve 1) is the value of Randall and Rossini.[14] Curves 2, 3, and 4 represent the partial specific heats of water in 0.5 m, 1.0 m and 2.0 m KCl. Rossini's 25°C values, which are believed to be accurate to 0.01%, were used as reference points, i.e., a parallel displacement of our curves was made so that they now run through Rossini's values. The curve AB is the specific heat of pure water, the line CB the ideal specific heat of water which does not contain Type Ice I molecules, according to Tammann.[11]

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[10] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," 37 (1923).

[11] Tammann: Z. anorg. Chem., **158**, 1 (1926).

It will be easier to understand the significance of these curves, if we know how the partial specific volumes in 0.1 m, 0.5 m, 1.0 m and 2.0 m KCl change with the temperature. For this reason, we have calculated the partial molal volumes of potassium chloride of Baxter and Wallace,[12] by plotting the volume of the solution against the molality and determining the slope of the tangents.[13] The partial specific volumes of water in these solutions, calculated from these values, are shown in Table IV.
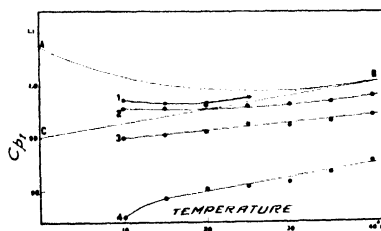
FIG. 2
Partial specific heat capacity of water in solutions of potassium chloride

TABLE IV

Partial Specific Volumes of Water in Solutions of Potassium Chloride

$\overline{V}_{p_1}$	0°C.	25°C.	50°C.	70°C.	100°C.
0.1 m KCl	.9997	1.0019	1.0121	1.0218	1.0430
0.5 m KCl	.99945	1.0022	1.0125	1.0223	1.0429
1.0 m KCl	.9987	1.0043	1.0133	1.0239	1.0414
2.0 m KCl	.9977	1.0085	1.0166	1.0273	1.0321

We have plotted these values of $\overline{V}_{p_1}$ against temperature in Fig. 3. AB is the specific volume curve of pure water. CB is the specific volume curve of water which is free from Type Ice I, according to Tammann's theory.[11] Curves 2, 3 and 4 are the partial specific volume curves for water in 0.5 m, 1.0 m, and 2.0 m KCl solutions. The dotted line represents 0.1 m KCl.

The specific heat data for potassium chloride could be checked directly with Rossini's work at 25° and accordingly they have been treated in detail. The rest of the electrolytes have been studied in a different manner. The partial specific heat of solvent water in molal solutions has been calculated in a simple manner by a recent method.[14,15] This method is particularly suitable when the number of concentrations for which data are available is rather limited. In this method the apparent molal heat capacity, Φ,[16] is plotted against the square root of the molality, $\sqrt{m}$. A smooth line results which is

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[12] Baxter and Wallace: J. Am. Chem. Soc., **39**, 70 (1916).

[13] Reference 10, p. 36.

[14] Randall and Rossini: J. Am. Chem. Soc., **51**, 324 (1929).

[15] Rossini: Bur. Standards J. Research, **4**, 316 (1930).

[16] Φ = (heat capacity of solution containing 1000 grams of water—heat capacity of 1000 grams of water) ÷ molality.
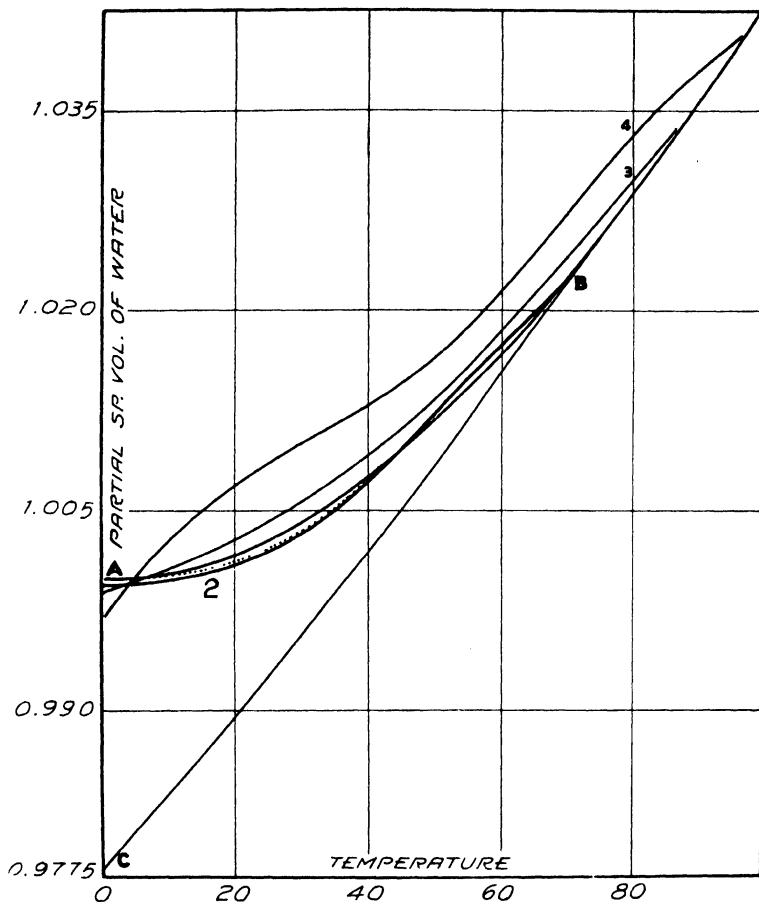
FIG. 3

Partial specific volumes of water in solutions of potassium chloride

often nearly straight over a wide range of concentration. The slope of this line $d\Phi/d\sqrt{m}$ at any concentration is an important quantity. It can be shown by simply differentiating Φ with respect to $\sqrt{m}$ and using the definitions of apparent molal heat capacity and partial molal heat capacity $\overline{C}_p$, that the difference between the partial heat capacity of a mol of solvent water in a large amount of solution, $\overline{C}_{p_1}$, and the heat capacity of a mol of pure water $\overline{C}^{\circ}_{p_1}$ (i.e. at infinite dilution) is given by the equation

$$\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1} = -\frac{m}{1000/18} \, 1/2 \, \sqrt{m} \, \frac{d\Phi}{d\sqrt{m}}$$

For 1 molal solutions $\overline{C}_{p_1} - \overline{C}^{\circ}_{p_1}$ is simply $-0.0090 \, d\Phi/d\sqrt{m}$. Dividing by 18.0 in order to change to the gram basis, the difference between the partial heat capacity of 1 gram of solvent water in solution and the heat capacity of 1 gram of pure water may be indicated as follows,

Specific heat$_{\text{Solvent water (1m.)}}$ $-$ Specific heat$_{\text{Pure water}}$ $= .00050\ d\Phi/dv\sqrt{m}$.

In Fig. 4, are shown graphs of Φ plotted against $\sqrt{m}$, calculated from the data of Table II. The smoothness (and approximate straightness) of such a line gives an exacting test of the consistency and reliability of the specific heat measurements. The errors are particularly magnified in dilute solutions and in these graphs it has been necessary to exclude the measurements of the 0.1 m solutions. The 35° curve for potassium acetate is not considered in the graph
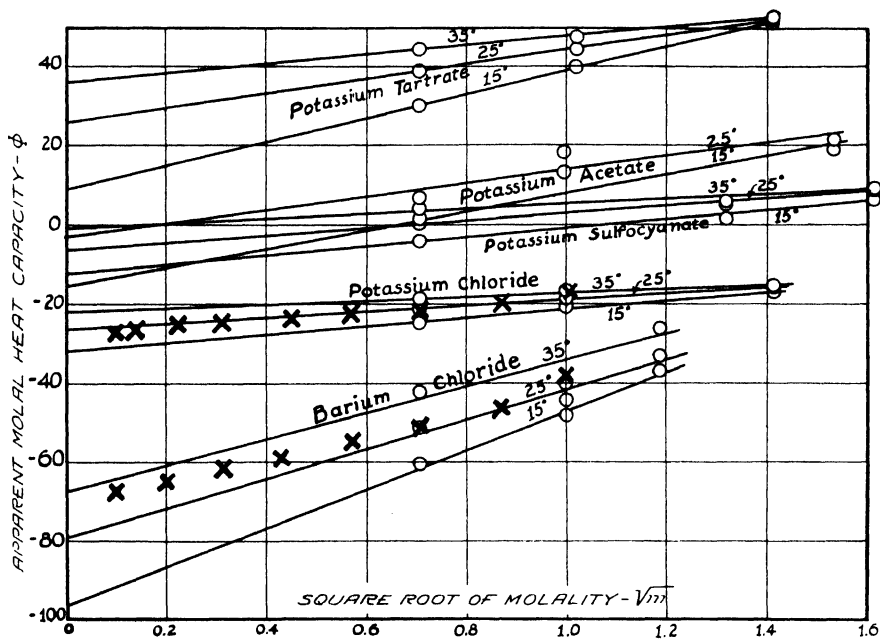
FIG. 4
Apparent molal heat capacity of water in solutions of electrolytes

because it would fall below the 25° curve, and such a phenomenon seems unlikely.

It is gratifying that where the results can be compared with other accurate work the agreement is excellent. The crosses in Fig. 4 for potassium chloride solutions at 25° are calculated from the determinations of Randall and Rossini;[17] the crosses for barium chloride at 25° are calculated from the determinations of Richards and Dole.[18] The slope of the curves drawn through these points at a concentration of 1 molal is practically identical with ours. The results of these other investigators show that, particularly in the case of barium chloride, the slope changes in the dilute solutions but in considering the shift of the water equilibrium we are concerned, primarily, with the more concentrated solutions.

Fortunately the scope of the present investigation can be extended with valuable data from the experimental data of Randall and Rossini[17] and with

[17] Randall and Rossini: J. Am. Chem. Soc., 51, 323 (1929).
[18] Richards and Dole: J. Am. Chem. Soc., 51, 724 (1929).

the data of Richards and his co-workers as recalculated by Rossini.[19]   In Table VI all of this material is grouped together. From the values of $\dfrac{(\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ})}{18}$ given in the third column and the known specific heat capacity of pure water one can easily calculate the heat capacity of one gram of solvent water in a large quantity of solution as shown in the last column.   In the next to the last column, the ions are arranged in the order of the lyotropic or Hofmeister series as determined from the salting out of inert gases and of proteins, and from various colloid phenomena.

TABLE V

Heat Capacity in Calories per Gram of Solvent Water in 1.0 Molal Solutions
of Electrolytes at 25°

Electrolyte	$\dfrac{d\Phi}{d\sqrt{m}}$	$\left(\dfrac{\overline{C}_{p_1} - \overline{C}_{p_1}^{\circ}}{18}\right)$	Lyotropic series	"Specific heat" of solvent water in 1 molal solution
Water	—	0	—	0.9985
BaCl$_2$	38	0.0189	Ba^{++}	0.9796
CaCl$_2$	24	0.0122	Ca^{++}	0.9863
K$_2$C$_4$H$_4$O$_6$	20	0.0100	SO$_4^{--}$	0.9885
K$_2$SO$_4$	11	0.0055	C$_4$H$_4$O$_6$	0.9930
KC$_2$H$_3$O$_2$	10	0.0050	C$_2$H$_3$O$_2^-$	0.9935
KCl	8.0	0.0040	Cl$^-$	0.9945
KNO$_3$	5.3	0.0025	NO$_3^-$	0.9960
KCNS	4.0	0.0020	I$^-$	0.9965
KI	3.3	0.0017	CNS$^-$	0.9968
NaCl	18	0.0089	Na$^+$	0.9896
KCl	8	0.0040	K$^+$	0.9945
Na$_2$SO$_4$	14	0.0072	Na$^+$	0.9913
K$_2$SO$_4$	11	0.0055	K$^+$	0.9930
NaNO$_3$	6.2	0.0031	Na$^+$	0.9954
KNO$_3$	5.3	0.0026	K$^+$	0.9959
NaI	3.8	0.0019	Na$^+$	0.9966
KI	3.3	0.0017	K$^+$	0.9968

The influence of temperature on the specific heat capacity of solvent water is shown in Table VI. It is not possible to find recent data for checking this temperature effect.

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[19] Rossini: Bur. Standards J. Research, **4**, 316 (1930).

TABLE VI

Influence of Temperature on the Specific Heat Capacity of Solvent Water
in 1 Molal Solutions of Electrolytes

Electrolyte	15°	25°	35°
Water	1.000	0.9985	0.9980
BaCl₂	0.9740	0.9796	0.9820
K₂C₄H₄O₆	0.9845	0.9885	0.9890
K₂C₂H₃O₂	0.9925	0.9935	—
KCl	0.9930	0.9945	0.9960
KCNS	0.9935	0.9965	—

Conclusions

Table VI shows that the idea back of the present investigation was justified
and that there is remarkable correlation between the order in which the ions
affect the heat capacity of water and the order in which they affect colloid
properties—i.e. the Hofmeister or lyotropic series. Those salts which come at
the head of the list decrease the heat capacity most and have the greatest
ability to salt out dissolved gases or proteins. As a direct result of this property
they lead to the highest temperature of gelation of certain colloids. A com-
parison of the effects of barium and calcium chloride shows that in 1 molal
concentration the barium ion is more effective than calcium ion, since the
chloride ions are the same in both.

The next seven salts all contain potassium ions and the differences in
behavior are due to the anions. Tartrate and sulfate which have the greatest
effect are divalent. All the others are univalent. The last group of eight salts
in Table V show conclusively that the effect of the sodium ion is always greater
than that of the potassium ion for any given anion.

These relationships are not evident when one examines only the heat
capacity per gram of solution. They are obscured by the changing of the
molecular weights and by other factors and are brought out only by the mathe-
matical relations which involve the way in which the specific heat of the solution
changes with the molality. The mathematical formula can be reduced to such
a simple form, however, that the order of the effect of electrolytes on the heat
capacity of water can be determined by a glance at the slopes of the lines,
$d\Phi/d\sqrt{m}$, in Fig. 4.

Thus barium chloride has the steepest slope and potassium sulphocyanate
the least. The former has the greatest effect on the heat capacity of water
and the latter the least and the other salts line up in their proper order.

The cause of the decrease in heat capacity of water by the presence of ions
is complicated. The intrinsic heat capacities of the ions themselves become
unimportant in the present method of calculating the partial molal heat
capacities of the solvent water. The charge of the ions serves to hold the water
molecules in a more rigid manner, restricting free movement of the units and
thus decreasing the degrees of freedom and diminishing the heat capacity of

the solvent water.   The divalent ions are, of course, more effective in this restriction than are the univalent ions.   The theoretical treatment of this effect of charge in very dilute solutions has been studied by other investigators. Hydration of the ions is a second effect which may be identical, in part at least, with the restriction of free motion due to the charge, already discussed. If the hydration becomes less as the temperature is raised there must be a tendency to increase the heat capacity on account of the absorption of heat in the process of breaking up hydrates.   This increase may more than offset the decrease in heat capacity caused by the decrease in the total number of separate units.

A third effect which may be called the depolymerization of water, we believe to be the most important factor in arranging the ions of a given charge in the order of the lyotropic or Hofmeister series.   It is generally believed that the abnormally high specific heat of water, the existence of a minimum heat capacity at $35°$ and a maximum density at $4°$ are due to the existence of polymers of water which break down with the absorption of heat as the temperature is raised.   It is immaterial for the present discussion whether these polymers are $(H_2O)_3$ or $(H_2O)_n$ or whether they are in the form of clusters of many molecules.   It seems likely that these polymers may be broken down also by the presence of electrolytes, and that part of the loss in heat capacity of water produced by the presence of the ions may be attributed to the loss of these heat-absorbing polymers.

Tammann[11] has sought to develop a quantitative theory for the behavior of water based on the depolymerization of polymers, (Type Ice I molecules). In Fig. 3 it will be noted that the specific volume curve of o.1 m KCl lies slightly below the AB line but that it merges with this line at $40°$.   According to Tammann's theory Type Ice I molecules have disappeared at $40°$ in pure water.   Therefore, at $40°$ and above, the partial specific volume curve of the solvent, and the specific volume curve of pure water coincide.   Curve 2 (o.5 M KCl) shows exactly the same effect.   Since curves 3 and 4 lie considerably above AB, it follows that the above explanation can be only partly true. Certainly the orientation of water molecules by the charged ions must be an important factor also.

The change in the condition of the solvent water by the addition of solutes is supported also by optical measurements.   Schade and Lohfert[20] observed a decrease in the intensity of the ultraviolet Tyndall cone of pure water upon the addition of electrolytes in o.1 N concentration.   They held that this decrease was caused by the depolymerization of Type Ice 1.   Gerlach[21] arrived at similar conclusions based on observations of the Raman bands of water.   The change in the Raman spectrum with temperature was similar to the change brought about by the additions of lithium chloride.

The influence of temperature on the partial specific heat capacity of solvent water is interesting.   The slopes, $d\Phi/d\sqrt{m}$, as shown in Fig. 4 become less as the temperature is raised from $15°$ to $35°$.   Thus, the difference between the

[20] Schade and Lohfert: Kolloid-Z., **51**, 65 (1930).

[21] Gerlach: Naturwissenschaften, **18**, 68 (1930).

heat capacity of the solvent water and pure water becomes less, i.e. the solvent water becomes more like pure water as the temperature is increased up to 35°. This fact is in accord with the suggestion that the electrolytes lead to the depolymerization of water, for if the temperature has already broken down some of these polymers there will be less opportunity for the electrolytes to do so. The temperature of minimum specific heat of water happens to fall at 35° and it would be interesting to have these measurements extended to a higher temperature range.

It is evident that the order of the slopes $d\Phi/d\sqrt{m}$ may not be the same at all temperatures and that the order of the ions may not be exactly the same as that shown in Table V for 25°. Furthermore, the lines in which Φ is plotted against $\sqrt{m}$ are often approximately straight but they are not necessarily so. Particularly in the very dilute solutions the slopes may change to such an extent as to alter C_p and change the order in which the ions affect the heat capacity of solvent water. It is predicted, then, that the lyotropic series or Hofmeister series can be influenced by temperature and concentration. Perhaps minor variations in the work of different investigators on the lyotropic series may be attributed to differences in concentration and temperature.

Summary

1. Specific heats have been obtained for solutions of barium chloride and of the potassium salts of hydrochloric, tartaric, acetic and sulfocyanic acids from 0.1 molal to 2 molal at temperatures from 10° to 40°C. Data have been obtained for 2 molal solutions of ammonium chloride and potassium bromide.

2. An adiabatic calorimeter was used with automatic control.

3. The partial specific heat capacities of the solvent water have been calculated for 1 molal solutions of several electrolytes.

4. The partial specific heats with potassium chloride have been calculated at several concentrations and compared with the partial specific volumes at different temperatures.

5. The order in which the ions decrease the heat capacity of the solvent water is practically the same as the order in which the ions appear in the lyotropic or Hofmeister series.

6. The presence of the electrically charged ions restricts the free motion of the water molecules and reduces the heat capacity. The depolymerization of water is suggested as a second factor in reducing the heat capacity, and arranging the ions of a given charge in the order of the lyotropic or Hofmeister series.

Laboratory of Physical Chemistry,
University of Wisconsin.

THE SYSTEM METHYL ALCOHOL–N-HEXANE AT 45 DEGREES*

BY JOHN BRIGHT FERGUSON

The system methyl alcohol–n-hexane was investigated at 45 deg. since Rothmund[1] had found the critical solution temperature to be 42.6 deg. Schukarew[2] determined the total pressures at 43.8 deg. and these and the solubilities are the only measurements which have been reported.

The differences which we encountered were those always associated with the use of anhydrous reagents. Rothmund stressed the importance of dry materials and our experiences amply confirmed his opinion.

Our apparatus was essentially that of Ferguson and Funnell[3] but to it was added a second sample tube container in parallel with the first. This enabled us to introduce the pure liquids into the apparatus. Had we prepared the two-component samples outside the apparatus, more hexane would have been required, contamination by water would have been greater and evaporation losses might have caused appreciable errors in the sample composition owing to the high vapour pressures of the solutions.

Our raw materials were Kahlbaum's best grade methyl alcohol and Eastman Kodak synthetic normal hexane. The alcohol was dried over freshly ignited lime for three weeks at room temperature, decanted off and distilled. In some cases, the alcohol was distilled over sodium in addition and in all cases care was taken to prevent contamination by water. The hexane was washed with 95 percent sulphuric acid until the acid layer remained colourless, with distilled water, with dilute alkaline permanganate solution and with distilled water in the order given. The hexane layer was separated and to it was added metallic sodium. It was left for two days but frequently shaken and then carefully distilled.

The temperature of the water bath was read on a Beckmann thermometer which had been compared with a standard. The vapour pressure of water at 45 deg. was found to be 71.9 mm; the value given in I.C.T. is 71.88 mm.[4] The vapour pressure of hexane was 333.0 mm which agrees with the value of 332.7 mm obtained from I.C.T.[5] and with the value 334.6 mm interpolated from the results of Thomas and Young.[6] For methyl alcohol we obtained a value of 327.9 as compared with 328 mm given by Ramsay and Young[7]

*An account of the results obtained by Messrs. Beare and McVicar and by Messrs. French and Wright.

[1] Rothmund: Z. physik. Chem., **26**, 433 (1898).

[2] Schukarew: Z. physik. Chem., **71**, 101 (1910).

[3] Ferguson and Funnell: J. Phys. Chem., **33**, 1 (1929); Beare, McVicar and Ferguson: **35**, 1068 (1931).

[4] Inter. Crit. Tables, **3**, 212 (1928).

[5] Inter. Crit. Tables, **3**, 222 (1928).

[6] Thomas and Young: Trans. Chem. Soc., **67**, 1071 (1895).

[7] Ramsay and Young: Phil. Trans., **178**, 313 (1887).

and for our stock hexane 325 mm. Schukarew's value of 309.5 mm for 43.8 deg. agrees with this last value and it would appear that either his hexane was impure or his temperature in error.

The critical solution temperature was determined by the sealed tube method. Our result was 42.4 deg.; Rothmund gives 42.6 deg.

The compositions of the co-existent vapour and liquid phases in the binary system were calculated from the determined vapour densities, the weights of the vapours and the weights of liquids introduced. The details may be found in earlier papers. However, there is one point which must be discussed here. N-hexane vapour is not a perfect gas and the two-component vapours are not perfect gaseous solutions. As a first approximation, it seemed probable that a knowledge of the behaviour of pure hexane vapour might suffice for the calculations. The useful method of treatment recently employed by Cope, Lewis and Weber[8] to correlate the densities of the vapours of the higher hydrocarbons did not yield results of sufficient accuracy nor did a consideration of the experimental results of Thomas and Young, of Ramsay and Steel[9] and of Hicks-Bruun.[10]

The results of Thomas and Young were extrapolated by plotting the observed volume of one gram divided by the corresponding volume calculated from the simple gas laws against the pressure. Hicks-Bruun states that the equation of Berthelot for limiting density is valid for unsaturated hexane vapour and the plot should yield a linear relation within narrow limits. The data, available, indicated that the observed volumes might deviate several percent from the calculated volumes and direct measurements seemed advisable. Our determinations are given in Table I.

TABLE I

Apparent formula weight of n-hexane

Temperature	Pressure	F.Wt.	Observer
48.6	334.1	88.34	Beare and McVicar
48.0	333.3	88.74	" "
49.7	331.0	88.47	French and Wright
		av. 88.5	

Subsequent experiments on the two-component system indicated that our determined vapour compositions would not differ greatly from each other and that the partial pressures would approach the vapour pressures of the pure liquids. When calculations were made using the formula weight for alcohol and the apparent formula weight for hexane just given, the partial pressures of hexane were found to exceed the vapour pressure of pure hexane in a number of cases. These improbable results forced us to calibrate our apparatus with known amounts of the pure vapours. For convenience, we calculated the apparent formula weight of hexane which we

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[8] Cope, Lewis and Weber: Ind. Eng. Chem., **23**, 887 (1931).

[9] Ramsay and Steele: Z. physik. Chem., **44**, 348 (1903).

[10] Hicks-Bruun: Bur. Standards J. Research, **5**, 575 (1930).

must use to get the right result when the normal formula weight of alcohol was assumed. Our best experiment gave these results: 49.4 deg., 548.5 mm, 75.21 wt. percent hexane; from initial weights—91.09, from weight condensate—91.35. Weight sample taken—5.9411, weight found—5.946, diff-0.0049. Two other experiments were not so satisfactory. One, 49.6 deg., 589.2 mm, 74.92 wt. percent hexane and the other, 49.7 deg., 587.6 mm, 74.37 wt. percent hexane gave respectively the values 90.95 and 90.38 from the weights of the condensates. From these, we concluded that a value, 91.1, would be probable one for this, our analytical constant. It was possible to use but one constant since the vapour compositions did not vary much from those used to determine this.

Our results are given in Table II. The mol. percentages are based upon 32.03 for methyl alcohol and 91.1 for n-hexane and the same units were used for the calculation of the partial pressures.

TABLE II

Liquid Composition		Vapour Composition			Partial Pressure		
Wt. % Hexane	Mol. % Hexane	Wt. % Hexane	Mol. % Hexane	Total Pressure	Hexane	M. Alcohol	Observer
18.06	7.18	72.51	48.1	611.0	293.9	317.1	F. & W.
19.27	7.74	71.96	47.45	601.7	285.6	316.1	,, ,,
20.15	8.15	71.90	47.39	606.9	287.6	319.3	,, ,,
22.0	9.02	73.89	49.86	617.2	307.7	311.5	B. & McV
24.88	10.43	73.47	49.30	618.1	304.7	313.6	F. & W.
28.92	12.51	73.48	49.30	624.1	307.7	316.4	B. & McV.
45.07	22.40	74.04	50.07	628.3	314.7	313.6	F. & W.
46.12	23.13	74.61	50.81	630.3	320.2	310.1	B. & McV.
72.95	48.67	74.06	50.12	630.2	315.8	314.4	,, ,,
89.86	75.82	74.49	50.67	626.4	317.5	308.9	,, ,,
95.72	88.63	75.16	51.56	619.3	319.3	300.0	F. & W.
98.35*	95.5*	79.87	58.28	549.8	320.4	229.4	B. & McV.
100	100	100	100	333.0	Average of detn. of F. & W. and B. & McV.		
0	0	0	0	327.9	F. & W.		

Temperature 45.00 ± 0.02°C.

*(Interp.)

The following results are shown graphically in Fig. 1: the total and partial pressures at 45 deg., the total pressures obtained by Schukarew at 43.8 deg. and the solubility curve of Rothmund.
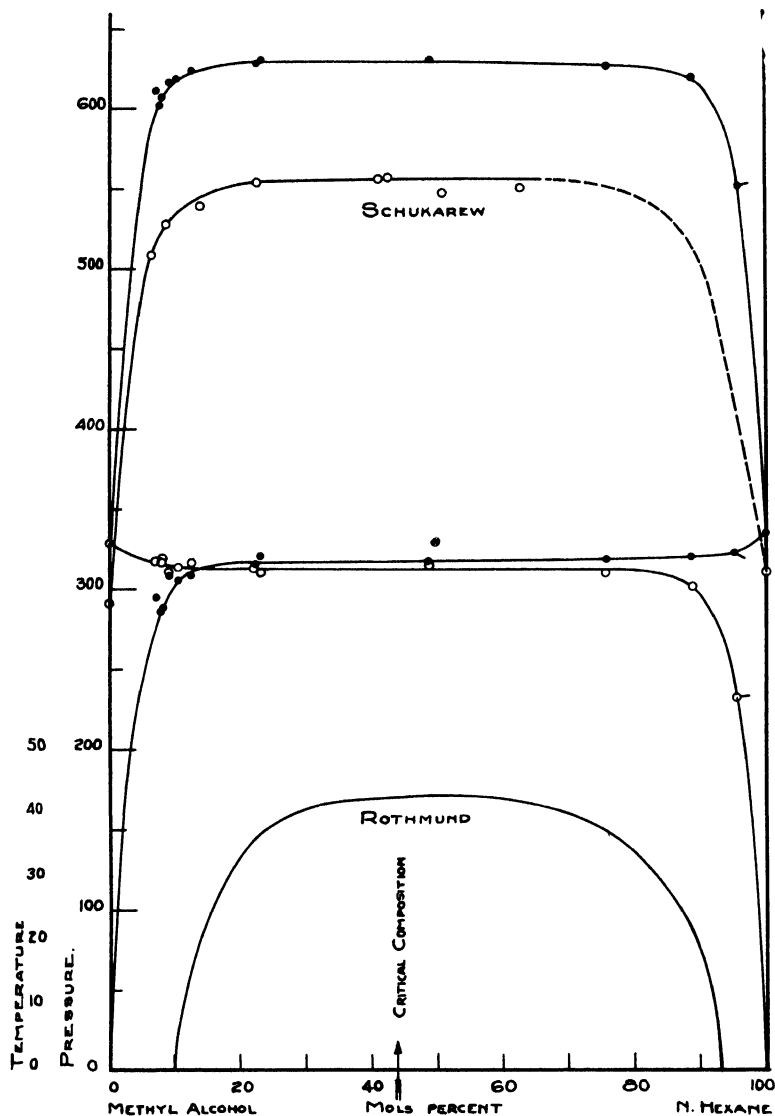
FIG. 1

Discussion

We have called 91.1 an analytical constant although later we have assumed it to be the formula weight of hexane in the vapour phases because we wished to stress the point that our results in weight percentages are independent of any theoretical significance which might be attached to this constant. The apparent formula weight of hexane probably varies from 86.11 for the dilute vapours, to 91.1 for the more concentrated vapours, finally reaching a value of 88.5 for the pure hexane, under our experimental conditions.

Obviously, only one value can be used for the presentation of these results in the customary manner and we have chosen 91.1. We have assumed that the methyl alcohol vapour was normal at all times although it is likely that this assumption is not strictly true. The high value chosen for hexane presents a problem. It seems unlikely that our value for pure hexane is too low since the sources of error other than contamination by water, would lead to higher results and if we ascribe it to the presence of water, we must conclude that it was easier to keep both alcohol and hexane dry than it was to keep hexane, itself. Our results indicate an appreciable volume change on mixing these vapours. It is an interesting fact that the apparent formula weight of hexane obtained from the two-component system is approximately equal to the value obtained by linear extrapolation from zero pressure through the vapour pressure of pure hexane to the vapour pressure of the solutions. This suggests that a study of such phenomena might shed some light on liquid phases in which the factors involved are more difficult to differentiate. One wonders whether such an effect occurs only in those systems, in which liquid immiscibility is found or may be easily produced.

The partial pressure curves are similar and do not indicate compound formation. They are not at variance with the Duhem-Margules equation although the comparison is, of necessity, crude and for theoretical reasons cannot be exact. The nearly horizontal portions of the curves extend over a wide range of liquid compositions which agrees with the results of others on similar systems and is also in accord with theory. The latter will be apparent from an inspection of the following equation given by Lash Miller:[11]

$$\mu_{xy} = \frac{\theta}{T}\mu'_{xy} - \frac{(\theta-T)}{T}\chi'_{xy} + \left\{(\theta-T) - \theta\log_e\frac{\theta}{T}\right\}C_{xy}$$

Since the change from an homogeneous to an heterogeneous system occurs over a small temperature range for an extended range of composition, it follows that μ'_{xy} must have a small value in order that the χ_{xy} and C_{xy} terms may be sufficient to give the value of μ_{xy} for the unstable homogeneous phase an opposite sign. If μ'_{xy} is very small, the corresponding partial pressures curves would be nearly horizontal, provided, as seems reasonable, that the deviations from perfect gaseous solutions are insufficient to affect this conclusion.[12]

On the other hand both χ_{xy} and C_{xy} cannot approach zero if μ_{xy} is to change sign on changing the temperature. Thus, the curves of χ and C cannot both be horizontal or linear over the range of compositions for which the partial pressure curves are nearly horizontal.

Such partial pressure curves cannot be explained by the judicious manipulation of the units used to express the liquid composition—a fact which is now generally admitted. One should not segregate such cases and assume that the factors, here important, are negligible in all other types of systems

[11] Lash Miller: Chem. Rev., 1, 327 (1925), Equation 9 but with terms rearranged.

[12] In a previous paper (Ferguson: J. Phys. Chem., 31, 762 (1927)), we presented similar deductions but used a slightly different equation.

nor accept, as proved, a degree of association the assumption of which enables one to correlate the experimental results by means of an equation. Siang Chieh Lee[13] has recently emphasized the importance of the "tendency to separate." We, also, believe that the theory of solutions will remain incomplete until a method has been found for the evaluation of the factor, mainly responsible for the nearly horizontal partial pressure curves in these extreme cases and probably important in many other cases as well.

Summary

1. The compositions of the co-existent liquid and vapour phases in the system methyl alcohol–n-hexane have been determined at 45 deg.

2. A study has been made of the densities of hexane vapour and of the two component vapour.

3. The total pressures and the calculated partial pressures have been given and the latter discussed.

Chemical Laboratory,
University of Toronto,
Toronto, Canada,
January 5th, 1932.

[13] Siang Chieh Lee: J. Phys. Chem., **35**, 3558 (1931).

THE LIESEGANG PHENOMENON APPLIED TO THE LAKE SUPERIOR IRON FORMATIONS*

BY ROBERT J. HARTMAN AND ROBERT McCULLOUGH DICKEY

Introduction

From an economic standpoint, the rock strata known as the Lake Superior iron formations are perhaps the most important natural deposits on the North American continent. To the geologist they afford innumerable and fascinating problems of structure and stratigraphy, of secondary ore concentration, and ultimately of origin. It is with the origin of this formation that this paper proposes to deal, but it will concern itself primarily with a single phase of a hypothetical process of origin, one which has either been completely overlooked heretofore, or which has been passed over with scant notice. The study lies within the legitimate province of the chemist, but his experimental work must be constantly limited by the geologic conditions either known definitely or strongly believed to have existed at the time of formation of these remarkable deposits. If it is possible for the structure and composition of the rocks comprising the iron formations to be synthetically reproduced in the laboratory, within the limitations imposed by the necessity of using only those elements in the reactions which could easily have existed in nature according to the most widely accepted geologic theories of origin, then a considerable advance will have been made. It is not proposed to enter into an involved discussion of the merits of the various hypotheses advanced by geologists to account for the deposition and occurrence of these rocks, except insofar as the results of the work described tend to support or disprove one or the other.

What are generally referred to as the iron formations are not in themselves iron ores. The iron formations proper were probably originally cherty iron carbonate and greenalite ($FeMgSiO_3.nH_2O$) which have undergone varying amounts of oxidation, leaching by circulating meteoric and magmatic waters, and metamorphism, leading to the production of minerals characteristic of these processes during the millions of years which have elapsed since their deposition. They vary from a few feet to one thousand feet in thickness, and contain roughly about 25% iron. The iron ores of the region have developed under favorable geologic conditions through the leaching out of the amorphous or finely crystalline silica of the iron formations and oxidation of the ferrous salts to hematite, limonite, and other of the varied forms of the higher oxides of iron. In short, the development of iron ore in these instances is the result of secondary concentration, through various agencies, of the iron in the primary iron formations.

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*Contribution from the Laboratory of Colloid Chemistry of Indiana University.

A peculiar and generally well-marked characteristic of these iron formations is their definite banding, which is particularly apparent in the rocks of some localities. Even a cursory examination suggests to the chemist the possibility of reactions in a silica gel having been of some importance in the formative processes. The iron carbonate, oxidized to different degrees, occurs in the iron formations in bands of varying thicknesses separated by other bands of chert, or silica. These bands exhibit no uniformity in thickness. Many attempts to explain this banding have been made, but all fall somewhat short of satisfying the conditions. It is true that no one explanation will suffice for the whole of the iron formations, since they were laid down over an area thousands of square miles in extent and were doubtless subject to the greatest differences in conditions. Nevertheless, it is entirely possible that one type of process may have been dominant, and the attempt to discover this certain type of process has occupied many geologists for a number of years.

Van Hise and Leith[1] assert that most of the iron salts and silica were contributed directly to marine waters by submarine basic lavas, that is, by direct contact of heated igneous material possessing a high ferromagnesian content, with the sea water. They show by a series of laboratory experiments that such a process is adequate to provide all the elements present in the iron formations, and their contention is supported by the close association in the Lake Superior region of vast amounts of weathered basic igneous rocks, greenstones and basalts, with the iron formations. Subordinate to this, they believe, was the weathering of the igneous rocks when cooled, leading to transportation to settling basins by meteoric waters of iron in the form of the ferrous salts of silicic, carbonic, sulphuric, hydrochloric, and other acids. They mention the fact that when iron silicates make contact with calcium carbonate, ferrous carbonate is precipitated, tending to agglomerate into bands separated by free silica.

Gruner,[2] on the other hand, contends that weathering of large land areas covered with greenstones and basalts was the predominant process. He postulates a humid climate, tropical or subtropical in nature, and abundant land vegetation of a low form affording rapid decay and solution of iron and silica as being of fundamental importance. According to his theory, most of the iron was carried to depositional basins as organic colloids or adsorbed by organic colloids, and was precipitated primarily through the influence of living algae and bacteria. Thus he subordinates inorganic reactions to organic.

An elaboration of the Gruner theory is offered by Maynard and Moore,[3] wherein they enter more thoroughly into the colloidal aspects. They contend that the banding is due to differential rates of precipitation of iron and silica, combined with seasonal changes causing varying quantities of these substances to be brought into the basins of deposition at different times of the

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[1] C. R. Van Hise and C. K. Leith: U. S. Geol. Sur., Mon. 52.

[2] Gruner: Econ. Geol., 17, 407 (1922); 18, 612 (1923).

[3] E. S. Moore and J. E. Maynard: Econ. Geol., 24, 272, 365, 506 (1929).

year. The emphasis of the banding, according to their idea, is due to meta-morphic processes, although the distinctness of the banding for the most part may be regarded as primary. They have produced banding of a rough order by differential settling in sea water of well-agitated ferric hydroxide and silica. Mention is made of the possibility of Liesegang's rings having been of some importance. They prepared a gel of equal volumes of 1.16 density sodium silicate and 3 N sulphuric acid which was made 0.1 N with respect to ferric chloride. The gel formed in a day or two, and was covered with ammonium hydroxide. In a month, ferric hydroxide bands developed. However, the authors claim that this process is inadequate to account for great thicknesses of the iron formation.

Experimental

The experimental work detailed in this paper tends to support the theories of Van Hise and Leith. It demonstrates conclusively that reactions in a silica gel will produce, under proper conditions, well-defined bands of ferrous carbonate, separated by silica bands. The banding peculiar to the iron formations is faithfully reproduced by this method. Briefly, the geologic considerations entailed are the presence of ferrous iron, non-oxidizing conditions in the gel tending to keep the iron in its ferrous form, sodium silicate, carbon dioxide (hence some form of life), and relatively quiescent conditions. All these can be reconciled with the direct submarine magma contribution theory. The sodium silicate and iron could readily have been supplied from the magma itself. Van Hise and Leith[1] found that when fresh basalt is heated to 1200° Centigrade, so that the surface is fused, and the mass is plunged into salt water, sodium silicate is produced, together with small amounts of iron salts.

Nitrogenous material and carbon dioxide may have been furnished by organisms; however, some of the carbon dioxide may have been supplied through action of the magma itself. Chamberlin and Salisbury[2] assert that carbon dioxide increases greatly in relative abundance with expiration of volcanic activity. If such is the case, most of this substance could have been supplied at a time when the period of violent igneous activity had passed and quiescent conditions had set in.

When the Simplon tunnel was dug through the Alps, the workmen cut through a vein of silicic acid soft enough to dig out with the hand.[3] It is the contention of the authors that this iron formation was no doubt at one time in similar gelatinous form and that while in this state a reaction, analogous to the Liesegang phenomenon, took place, giving rise to the ferrous carbonate bands. Dehydration, pressure, etc., through the ages leaves the iron formation in its solid state with its ferrous iron having been trapped and isolated from air, preventing it from further oxidation.

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[1] C. R. Van Hise and C. K. Leith: U. S. Geol. Sur., Mon. **52**, 516.

[2] Chamberlin and Salisbury: "Text-Book of Geology," **1**, 590 (1904).

[3] Holmes: "Laboratory Manual of Colloid Chemistry," p. 136.

Of importance in this connection, it may be observed here that the authors have found that passage of carbon dioxide gas through sodium silicate solution will cause it to form a very firm silicic acid gel in a short time.

From approximately seventy-five different experimental preparations, the fifteen showing the best banding are pictured in Plate I.

The first horizontal row of test tubes (A) in Plate I contains gels prepared by mixing equal volumes of 1.06 density water glass and normal ammonium carbonate solution. The horizontal row, B, consists of gels formed by mixing equal volumes of 1.06 density water glass and 0.8 N ammonium carbonate solution. The test tubes in the third horizontal row, C, contain gels prepared by mixing equal volumes of 1.06 density water glass and 0.5 N ammonium carbonate solution.

The row A gels set in approximately five minutes, the row B gels in ten minutes, and the row C gels in an hour.

In order, from left to right, to the first test tube in each horizontal row was added approximately seven cubic centimeters of 0.1 N ferrous ammonium sulfate solution. To the second test tube in each horizontal row was added the same amount of 0.3 N ferrous ammonium sulfate solution, to the third 0.5 N ferrous ammonium sulfate solution, to the fourth 0.8 N ferrous ammonium sulfate solution and to the fifth normal ferrous ammonium sulfate solution.

The ferrous ammonium sulfate solutions were changed once each day for three days, and then were replaced twice daily for three days. Following this they were permitted to stand untouched for three days, at the end of which time the photographs were made.

Due to the oxidation of the ferrous salt, it was found necessary to use in each instance freshly prepared solutions of ferrous ammonium sulfate of identical concentrations.

Test tubes containing the same respective concentrations of ammonium carbonate in the gels and of ferrous ammonium sulfate in the solutions above the gels (as in Plate I) were prepared, and allowed to stand without replacing the ferrous ammonium sulfate solutions. It was found that ferrous carbonate bands formed. However, those bands formed when the ferrous ammonium sulfate solutions were changed at regular intervals were more numerous and more distinct.

Since the photographs were taken (three weeks), the gels below the bands have in most instances become grayish-white in color almost to the bottoms of the test tubes, without, however, formation of any bands other than those pictured. This is probably due to the diffusion of ferrous carbonate throughout the gel.

Concentrations of ferrous ammonium sulfate lower than 0.1 N failed to produce bands. Equal volumes of 1.06 density water glass and 0.3 N ammonium carbonate solution were mixed and a gel set in approximately one hundred hours. This gel was unsatisfactory for use, as shrinkage due probably to evaporation over a long standing period gave rise to cracks at the surface
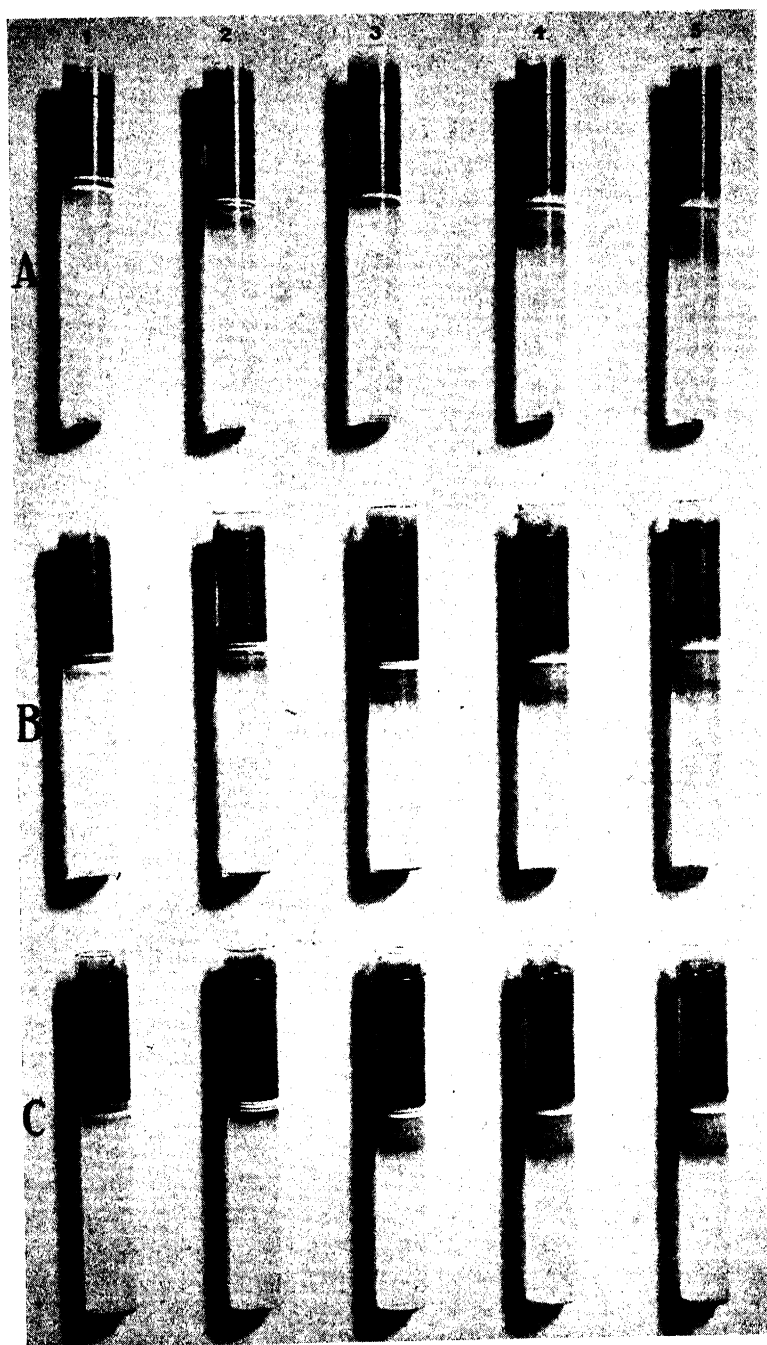
PLATE I
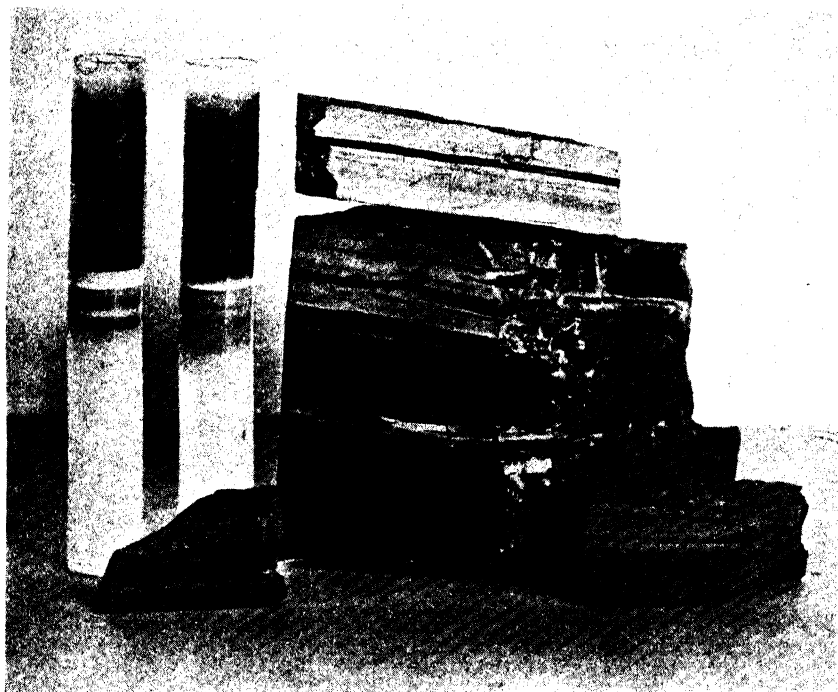
PLATE II

of the gel.   Concentrations of ammonium carbonate solution less than 0.3 N
did not produce gelation upon mixing with an equal volume of 1.06 density
water glass.

From a comparison of the tubes in Plate I, it may be said that no general
relationship between the concentration of ammonium carbonate in the gel
and distinctness and number of bands formed may be deduced.   With
increasing concentration of ferrous ammonium sulfate in the solution placed
above the gel, it can be stated that the bands become wider, and less sharply
defined.   This may be observed in each horizontal row of tubes, where the
concentration of the soluble iron salt increases from left to right.

It is interesting to note that some very white bands of ferrous carbonate
occur in the gels.   The unusual lightness of these bands is probably due to
the fact that they are formed in the absence of air.

Plate II shows four separate specimens of the iron formation from the
Crystal Falls district of Michigan, whose faces have been polished so as to
better reveal the structure.   For purposes of comparison, two test tubes
illustrating banding of the type produced in the laboratory have been in-
cluded.   As may readily be seen, the similarity between the synthetic and
the natural products is very marked.   The banding in the tube on the left
was formed in a gel composed of equal volumes of 0.5 N ammonium carbonate
solution and 1.06 density water glass, and placing over this a solution of

ferrous ammonium sulfate to which was added approximately 0.5 grams of ferrous ammonium sulfate crystals daily for five days. The bands in the tube on the right were formed in the same manner, with the difference that the gel was prepared of equal volumes of normal ammonium carbonate and 1.06 density water glass.

Conclusion

In short, then, the authors contend that the peculiar banding of the iron formations, in some localities, has been brought about by slow diffusion of soluble ferrous salts through a gel formed by the interaction of basic nitrogenous substances, carbon dioxide, or carbonates with sodium silicate, giving rise to irregularly spaced bands of varying thicknesses of insoluble ferrous carbonate separated by silica. It is the opinion of the authors that in many cases this is the most logical explanation of the formation of the rock structure in question. Further work concerning the application of the Liesegang phenomenon to the geology of this iron formation is being carried out by the latter author while the former is making further study of the formation of ferrous carbonate bands in gels.

A COMPARISON OF COLORIMETRIC AND ELECTROMETRIC METHODS IN THE DETERMINATION OF pH VALUES OF VARIOUS GELATIN SOLUTIONS*

BY R. J. HARTMAN AND I. F. FLEISCHER

Introduction

The colorimetric methods have been resorted to almost entirely by investigators and by manufacturers in determining the pH value of various gelatin solutions. Walter S. Hughes,[1] however, measures the potential of a 1% gelatin solution by means of a glass electrode and a hydrogen electrode. The potential of this solution is changed by the addition of sodium hydroxide and hydrochloric acid solutions. A curve is then obtained by plotting the potential measured by the hydrogen electrode against that of the glass electrode. A similar curve is constructed from measurements of a solution where no gelatin is present. The former curve assumes the general shape of the latter but the potential measured by the glass electrode gives values lower than in the case where gelatin was not present. This phenomenon is explained by stating that the presence of gelatin produces substances other than hydrogen-ions which affect the glass surface potential. It is further asserted that before any acid or alkali was added to the gelatin solution the glass surface potential was 0.531 and the hydrogen potential 0.560. This difference is accounted for by saying that the presence of electrolytes has some influence on the adsorption of gelatin on the glass surface. It was further found that the potential measured by the glass surface electrode depends upon both the nature of the solution and the time of contact.

Allen E. Stearn[2] has studied the nature of isolectric gelatin in solution. It was found that when a solution of a certain pH value was mixed with a basic dye of the same pH value, there was a very significant decrease in pH. The opposite was noted with acid dyes. In explanation two apparent mechanisms are presented.

$$DCl + HGe = DGe + HCl$$

or better

$$D^+ + HGe = DGE + H^+$$
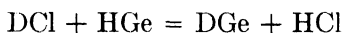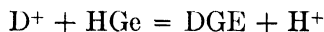
where D^+ is the dye cation and Ge the gelatin radical. An adsorption mechanism depending on the equilibrium is the other explanation offered.

$$DCl + HOH = DOH + HCl$$
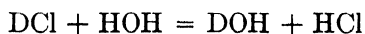
It is definitely shown by Stearn that, when an acid dye reacts with a gelatin solution, the hydrogen-ions from the protein molecule are used up or, in the

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[1] Hughes: J. Am. Chem. Soc., **44**, 2860 (1922).
[2] Stearn: J. Phys. Chem., **34**, 973 (1930).

case of a basic dye, hydroxyl-ions are used up. The disappearance of ions from a gelatin solution upon the addition of crystal violet (basic dye) is shown by a decrease in the conductivity of such solution.[3] It would have been indeed interesting had the two investigators above mentioned compared the pH values they obtained by potentiometric methods with values obtained from colorimetric indicators.

Stearn has conclusively shown that a gelatin molecule in solution combines chemically with either an acid or basic dye. From this it is reasonable to assume that in the colorimetric determination of the pH value of a gelatin solution the indicator chemically unites with the gelatin molecule arresting any free acid or basic ions due to the hydrolysis of a gelatin in solution. The work of Stearn indicates the existence of an ampholyte ion in gelatin solutions. This ion would, accordingly, prevent equilibrium in potentiometric determinations since it would not be combined chemically and would be free to react with other ions in solution.

This investigation was undertaken to compare the pH values obtained from two colorimetric methods with those obtained from three potentiometric methods and to study the variation of values yielded from the potentiometric methods with time, or, the time necessary for equilibrium.

Experimental

Material used. The hide glue used in this investigation was furnished through the courtesy of Conrad-Kammerer Glue Company, New Albany, Indiana, the bone glue through the courtesy of Armour Glue Company, Chicago, Illinois. The casein glue was prepared in this laboratory by the grain-curd process. The vegetable glue was prepared in this laboratory by digesting on a boiling water bath 50 grams of tapioca flour with 150 cubic centimeters of water containing 5.6 grams of caustic soda and then adding 5-100 cc. portions of water. This material was dried in an oven between 40-50° C. over night. The dry product was granulated for use.

The solutions to be tested were prepared in the following manner:

Two grams of the gelatin was allowed to soak in water over night and then heated to 62°C. at which temperature the solution became homogeneous after a 15 minute period. The solution was then permitted to come to room temperature. Ten cubic centimeter portions were used in all colorimetric determinations while fifty cubic centimeter portions were used in all potentiometric determinations with readings at definite time intervals. Redistilled water was used throughout the entire investigation.

Equipment. The pH of each gelatin solution was first determined using Clark and Lubs standard colorimetric indicators. The indicators were obtained from Coleman and Bell Company, Norwood, Ohio. The Hellige Colorimetric Comparator was also used in determining the pH value. This comparator and the standard indicator solutions were obtained from the Hellige

[3] Reference 2, p. 981.

Klett Company, Inc., New York, New York. In each instance the two colorimetric methods gave the same pH value.

The three electrodes used in the potentiometric methods were the hydrogen, quinhydrone and glass, each in combination with a saturated calomelhalf cell. With the hydrogen and glass electrodes Leeds and Northrup hydrogen-ion potentiometer (no. 7665) was used. Leeds and Northrup quinhydrone pH indicator (no. 7654) was used in making determinations with the quinhydrone electrode. The quinhydrone and hydrogen electrodes were obtained from the same company.

The glass electrode was prepared by welding a very thin sheet of glass to a piece of glass tubing about 10 centimeters long and 1.5 centimeters in diameter as shown in Fig. 1. The thin sheet of glass was prepared by blowing a large thin-walled bulb from a piece of soda glass tubing.

The lower end of the glass was heated to dull red heat when it was pressed against the thin sheet of glass, which was placed on a piece of clean asbestos slate. Tests were made for leakage by filling the tube with saturated potassium chloride solution.

The hydrogen used with the hydrogen electrode was electrolytic hydrogen purified by passing through a train consisting of hot copper, concentrated sulphuric acid, glass wool and caustic soda sticks.

A convenient and inexpensive saturated calomelhalf cell was devised by using a small clean wide mouth bottle arranged as shown in Fig. 2.

Data. Table I shows the values of E.M.F. and pH obtained by the various methods with the different gelatins. In carrying out the potentiometric determinations, readings were taken at various time intervals in an attempt to determine the length of time for equilibrium to take place in the solution. Horizontally is listed the various gelatins studied while vertically the E.M.F. and pH values are given with the time of reading. All of the readings were taken over a temperature range of 24 to 30°C. Correction for same was made in the calculation of each pH value.

From the following table it is noted that the two colorimetric methods, Clark and Lubs, and Hellige, gave identical pH values. The results obtained from the hydrogen electrode of each gelatin can in no way be compared with the value obtained from the colorimetric methods. At the expiration of 60 minutes in the potentiometric determination of the hide gelatin, a value
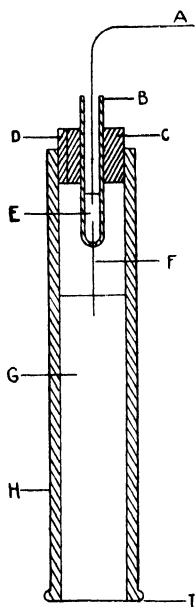
FIG. 1

A Copper wire.
B Glass tube.
C Cork.
D Groove in cork C to prevent pressure inside electrode.
E Mercury.
F Platinum wire.
G Saturated KCl solution.
H Glass tube 10 cm. long and about 1.5 cm. in diameter.
I Thin sheet of glass.
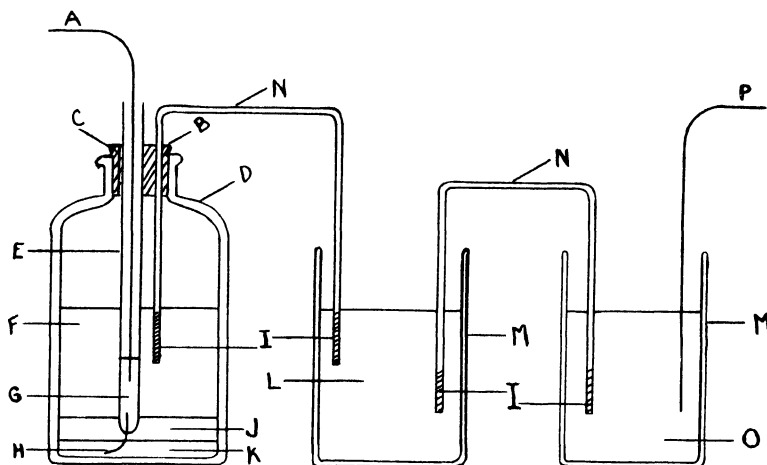
Fig. 2

A   Copper wire.
B   Cork.
C   Groove in cork B to prevent pressure inside cell.
D   100 cc. wide mouth bottle.
E   Glass tube.
F   Solution saturated with respect to KCl and calomel.
G   Mercury.
H   Platinum wire.
I   Agar gel or crushed filter paper.
J   Calomel paste.
K   Mercury.
L   Saturated KCl solution.
M   100 cc. beaker.
N   Saturated KCl bridge.
O   Solution to be tested.
P   Opposite electrode.

similar to that received with the colorimetric indicators is obtained. Since, however, the values received prior to the expiration of 60 minutes were much less than 6.6, and, since those values received after expiration of 60 minutes were greater than 6.6, this fact is coincidental.

In general, the pH values obtained with the quinhydrone electrode did not vary with time to the same extent as the values obtained from the hydrogen electrode.

Apparent equilibrium was reached in the quinhydrone determinations of the hide and casein gelatins after about 25 minutes. The values obtained at this point, however, are quite different from those obtained by the colorimetric indicators. The pH value obtained from the quinhydrone electrode with bone gelatin at the expiration of 40 minutes compared with that obtained with the two colorimetric methods. Since, however, the pH values continued to vary before and after the expiration of 40 minutes, this again may be considered coincidental.

The pH values obtained from the glass electrode did not vary with time to the same extent as the values obtained from the hydrogen electrode and in each case the pH values obtained from this method were very much lower than those obtained by the colorimetric methods.

TABLE I

Comparison of EMF and pH Values of Different Gelatin Solutions as measured by Various Methods

Gelatin	Bone			Hide		
Colorimetric pH values by Clark and Lubs, and Hellige Comparator	5.6			6.6		
	Time in Minutes	EMF Volts	pH Calculated	Time in Minutes	EMF Volts	pH Calculated
Hydrogen	15	.0707	——	5	.2513	0.143
Electrode	19	.0224	——	10	.5427	5.007
	28	.2360	——	15	.5980	5.930
	37	.4477	3.55	30	.6120	6.160
	53	.5356	4.89	45	.6180	6.260
	65	.5410	4.98	60	.6220	6.580
	83	.5476	5.28	130	.6418	6.920
	103	.5439	5.01	235	.6473	7.020
	123	.5449	5.04			
	280	.4144	2.86			
Quinhydrone	5	−.126	5.35	5	−.1210	5.60
Electrode	20	−.123	5.45	12	−.1235	5.65
	40	−.118	5.60	23	−.1235	5.65
	60	−.120	5.50	44	−.1220	5.60
	215	−.122	5.55	85	−.1210	5.60
				120	−.1210	5.60
Glass	5	.3299	(2)	5	.1150	(2)
Electrode	14	.3141		20	.1263	
	26	.3268		40	.1336	
				55	.1350	
		Electrode		75	.1336	
		Fractured		100	.1324	
				115	.1297	
				120	.1289	

TABLE I (Continued)

Comparison of EMF and pH Values of Different Gelatin Solutions as measured by Various Methods

Gelatin	Casein			Vegetable		
Colorimetric pH values by Clark and Lubs, and Hellige Comparator	4.0			9.0 (Phenol phthalein) (Hellige comparator not used)		
	Time in Minutes	pH EMF Volts	Calculated	Time in Minutes	EMF Volts	pH Calculated
Hydrogen	10	.4101	2.78	1.5	.1000	—
Electrode	20	.4173	2.91	5.0	.4243	3.19
	25	.4201	2.95	10.0	.6843	7.38
	35	.4242	3.01	15.0	.8087	9.46
	50	.4244	3.02	30.0	.8185	9.62
	60	.4250	3.03	48.0	.8187	9.63
	75	.4253	3.04	80.0	.8170	9.60
	90	.4256	3.05	100.0	.8167	9.58
	105	.4258	3.05	120.0	.8162	9.57
	120	.4270	3.07			
	180	.4274	3.19			
Quinhydrone	5	−.3240	2.15	28	.2540	(1)
Electrode	10	−.3290	2.07	75	.2558	
	25	−.3320	2.05	95	.2589	
	46	−.3330	2.02	120	.2408	
	62	−.3330	2.02			
	108	−.3335	2.02			
	128	−.3335	2.02			
Glass	7	.3214	(2)	5	.0867	(2)
Electrode	10	.3302		10	.1320	
	17	.3290		15	.1419	
				30	.1221	
	Electrode			45	.1301	
	Fractured			60	.1391	
				80	.1574	
				105	.1382	
				120	.1426	

(1) It is known that the quinhydrone electrode will not give correct values for pH when the alkalinity is pH = 9 or greater.

(2) The pH values were not calculated in this case due to the fact that sufficient information is not available.

The accuracy of the pH determinations does not seem to vary with gelatins made from different materials.

In view of the fact that the readings obtained potentiometrically in no case reached a constant value, it is apparent that equilibrium in solution is not obtained. This quite likely could be due to the existence of an ampholyte ion in solution. This ampholyte ion may form inner salts or react with other ions which are no doubt in solution as impurities. In the colorimetric determination this ampholytic ion is probably united chemically with the organic indicator, thus yielding pH values more correct and constant.

If the variations of the pH values with time is due to an ampholytic ion, which is probably the case, equilibrium would not be expected in unbuffered solutions such as those tested. Values of pH constant with time also agreeing with the colorimetric values could be probably obtained if the solutions could be buffered. Further work along this line conducted by the authors will appear in a later issue of this journal.

Conclusion

1. The pH values obtained from the glass, quinhydrone and hydrogen electrodes in the potentiometric determination of the various gelatin solutions do not agree with the pH values obtained colorimetrically.

2. Of the methods employed in this investigation, only the colorimetric methods can be relied upon.

3. There was no equilibrium reached in the potentiometric determination of the gelatin solution over the period of time studied.

4. The data indicates the existence of ampholyte ions in each of the gelatin solutions studied as first pointed out by Stearn.

5. Of the three electrodes studied, the pH values obtained with the quinhydrone electrode seemed to give readings most constant with time, but these values did not agree with the colorimetric determinations.

THE ENTROPY OF STEAM, AND THE WATER-GAS REACTION

BY A. R. GORDON AND COLIN BARNES

The Entropy of Steam and the Water-Gas Equilibrium

A knowledge of entropies provides the most direct method of obtaining free energies of reaction, equilibrium constants, etc. from purely thermal data. The entropies of many diatomic gases at moderate temperatures have now been calculated from the formulae of quantum mechanics and the data of spectroscopy, and a few polyatomic molecules have been treated as symmetrical rotators, a structure of limited applicability.

The entropy of steam is of fundamental importance in many thermodynamic problems, but so far the calculation has not been made for such an asymmetrical top. In this paper we shall compute the entropy, and check the result against the experimental values of the free energy and heat of formation of water. A second check on our value can be obtained from the water-gas reaction whose equilibrium constant is now accurately known. Values of the entropy obtained by using an "effective" moment of inertia[1] have been previously employed to determine the "integration constant" for this reaction, but a more exacting test is to calculate the equilibrium constant itself, which, after all, is the quantity given directly by experiment. This latter calculation requires also the entropies and heat capacities of hydrogen, carbon monoxide and carbon dioxide for temperatures from $600°K.$ to $1200°K.$ These three gases are treated by a uniform method applicable to diatomic (and pseudo-diatomic) gases, and since the process[2] is now a familiar one, only a very brief description of the essential points in the calculation is given. The heat capacities are computed and tabulated with the accuracy necessary for the calculation of the water-gas equilibrium; the so-called experimental values[3] are of no use; they still need a critical revision and a sharp distinction between laboratory values and numbers derived by extrapolation.

As is usual, we get the contributions to the entropy of steam from the translational, vibrational and rotational parts of the energy. We believe that for this molecule the process gives reasonably good results up to $1200°K.$, though of course the interactions must eventually be taken into account. If the energy state ϵ_n occurs with the weight p_n we define the "state-sum" Σ_1 and the "energy-sum" Σ_2 by

$$\Sigma_1 = \sum_n p_n \cdot e^{-\epsilon_n/kT} \tag{1}$$

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[1] See for example Eucken: Physik. Z., **30**, 818 (1929).

[2] See for example Rodebush: Chem. Rev., **9**, 319 (1931).

[3] Inter. Crit. Tables, **5**, 79. This point has already been noted by Bryant: Ind. Eng. Chem., **23**, 1019 (1931).

$$\Sigma_2 = \sum_n p_n \cdot (\epsilon_n/kT) \cdot e^{-\epsilon_n/kT} \qquad (2)$$

The entropy is then

$$S = R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \qquad (3)$$

Here ϵ_n is the energy of a vibrational or rotational state. The translational entropy is given by the usual Sackur-Tetrode expression corrected where necessary for the deviation of the gas from ideality.

We have used the following values of the constants:[1] $R = 1.9858$ cals./deg.; $k = 1.372 \times 10^{-16}$ ergs/deg.; $h = 6.55 \times 10^{-27}$ ergs/sec.; $N = 6.06 \times 10^{23}$; 1 atmosphere $= 1.0133 \times 10^6$ dynes/cm.[2] All temperatures are in degrees Kelvin, pressures in atmospheres, and entropies and heat capacities in cals./deg.

§ 1: The Translational and Vibrational Entropy of Steam.

The translational entropy is given by the familiar expression

$$S_T = R \ln[(2\pi/h^2N)^{3/2} \cdot k^{5/2} \cdot e^{5/2}] + 5R/2 \ln T - R \ln P + 3R/2 \ln M + s \qquad (4)$$

where M is the molecular weight in grams, s is the correcting term for deviation from ideality, and the other symbols have their usual significance. To compute s, we used the equation of state for water vapour given by Steinwehr;[2] the magnitude of s is obvious from a comparison of the entries in the second and third columns of Table II; at 300° for saturated steam it amounts to -0.003 in the entropy, while for 400° and 1 atmosphere it is about ten times as great.

There must be three fundamental frequencies in the vibration spectrum of the H_2O molecule; two of them are reasonably certain, the third is doubtful. Fortunately, the smallest frequency, which is by far the most important, is fairly accurately known. We adopted the values of Mecke[3]

$$\omega_1 = 3930 - 95_{n_1} \qquad \omega_2 = 3950 - 100_{n_2} \qquad \omega_3 = 1600 \text{ cm}^{-1}.$$

The corresponding energy levels are

$$hc(n_1\omega_1 + n_2\omega_2 + n_3\omega_3)$$

There are no weight factors when the summations involved run over all possible zero and integral values of n_1, n_2 and n_3. The contributions at the various temperatures are listed in the column headed S_V in Table II. At 1200° the vibrational entropy amounts to 1.215 with perhaps an error from the uncertainty in the frequencies of five per cent, while at 300° the vibrational entropy is only 0.008.

§ 2: The Rotational Entropy of Steam.

The H_2O molecule, so far as rotational states are concerned, is an asymmetrical top; its three principal moments of inertia are not known very accurately, and we selected the values 0.98×10^{-40}, 1.80×10^{-40} and 2.80×10^{-40}, given by Mecke.[4] Fortunately, a moderate change in the moments of inertia

[1] Standard table (1926) Handbuch der Physik.
[2] Steinwehr: Z. Physik, 3, 466 (1920).
[3] Mecke: Physik. Z., 30, 907 (1929).
[4] Mecke: Trans. Faraday. Soc., 26, 214 (1930).

causes only a relatively slight change in the entropy; for example, the use of Bailey's values[1] (0.97×10^{-40}, 1.91×10^{-40}, 2.91×10^{-40}) would lead to a rotational entropy only 0.09 higher than that entered in Table I.

The energy levels of an asymmetrical rotator are now well known; the equations for the first nine sets $J = 0$ to $J = 8$ have been conveniently summarized by Dennison,[2] and need not be given here. The energy depends not only on J but also on a subsidiary number τ which takes the $2J+1$ values $-J$, $-J+1$, $-J+2$, . . . $J-1$, J. As regards the symmetry of the rotational states, we have (for even values of J) symmetrical levels $\tau = -J$, $-J+2$, . . . and antisymmetrical levels $\tau = -J+1$, $-J+3$, . . . while for odd values of J, the levels $\tau = -J$, $-J+2$, . . . are antisymmetrical and the levels $\tau = -J+1$, $-J+3$, . . . are symmetrical.[3] Moreover each level has the usual weight $2J+1$. In addition, the symmetrical and antisymmetrical rotational states must be weighted differently on account of the two hydrogen atoms, each with nuclear spin, in the molecule; the relative weights here are 3 and 1. It makes no practical difference (less than 0.001 in the entropy) whether the symmetrical or antisymmetrical states are given the weight 3, a circumstance which justifies the separate treatment of the vibrational contributions, for the symmetry of the vibrational part of the wave function changes for every change by unity in the quantum number n_3. In our calculation, we gave the complete weights $3(2J+1)$ to the symmetrical rotational levels and $2J+1$ to the antisymmetrical.

The rotational energy levels $\epsilon_{J\tau}$ for $J = 0$ to $J = 8$ were found by solving the exact equations;[4] for higher J values asymptotic formulae were used.[5] It may be of interest for subsequent calculations to sketch briefly the use of these formulae. From the levels $J = 8$, the quantity

$$\lambda_0 = 8\pi^2 \cdot \epsilon_{J\tau}/h^2 J(J+1) \tag{5}$$

is plotted against $(J + \tau + 2\beta)/(J + 1/2)$ where $\beta = 0$ for $\tau = J$, $J - 2$, . . . and is equal to $1/2$ for $\tau = J - 1$, $J - 3$, . . . From this graph we can

[1] Bailey: Trans. Faraday. Soc., 26, 203 (1930).

[2] Dennison: "Reviews of Modern Physics," 3, 280 (1931).

[3] This assignment of symmetry and antisymmetry to the rotational part of the wave function corresponds to Dennison's case b (loc. cit. p. 332) and assumes that the intermediate moment of inertia lies along the axis of symmetry of the molecule (cf. Mecke: Trans. Faraday Soc. 26, 214). If the smallest moment of inertia were assumed to lie along the axis of symmetry, as in Eucken's early model for the water molecule, Dennison's case a would apply, and for either odd or even J, the levels $\tau = -J$, $-J+3$, $-J+4$, . . . would be symmetrical, and the levels $\tau = -J+1$, $-J+2$, $-J+5$, $-J+6$, . . . would be antisymmetrical. As far as the calculation of the entropy is concerned, either a or b leads to the same numerical value for 300° within 0.002.

[4] The actual levels in wave numbers are given below; they may be of interest as showing the general distribution of the levels for such an asymmetrical top.
$J = 0$: 0. $J = 1$: 25.2, 38.1, 43.6. $J = 2$: 74.3, 83.1, 99.5, 138.1, 139.5. $J = 3$: 144.9, 149.8, 182.5, 213.8, 220.4, 292.6, 292.8. $J = 4$; 235.0, 237.5, 290.8, 315.3, 330.8, 395.8, 397.4, 501.4, 503.3. $J = 5$: 344.7, 345.7, 422.1, 436.7, 470.3, 524.9, 530.8, 632.4, 632.7, 769.9, 769.9. $J = 6$: 473.6, 474.0, 574.0, 582.1, 637.3, 679.4, 694.5, 788.3, 789.7, 925.0, 1093.1, 1093.1. $J = 7$: 622, 625, 731, 745, 823, 858, 889, 980, 1001, 1106, 1107, 1272, 1273, 1473, 1473. $J = 8$: 790, 790, 934, 937, 1042, 1061, 1113, 1179, 1194, 1316, 1317, 1478, 1482, 1679, 1679, 1909, 1910.

[5] Kramers and Ittmann: Z. Physik, 58, 217 (1929).

read off values of λ_o, and hence of $\epsilon_{J\tau}$, for higher values of J and for positive values of τ not too near zero. Another graph of the same two quantities but with $\beta = 1/2$ for $\tau = -J, -J + 2, \ldots$ and $\beta = 0$ for $\tau = -J + 1, -J + 3,$ $\ldots$ gives the value of λ_o for negative values of τ not too near zero. Finally, the values of λ_o for τ equal to or near zero are found directly from Eq. 47 of Kramers and Ittmann.[1] The graphical method gives the mean positions of the pairs into which the rotational states fall for high J's, and for the present purpose it is unnecessary to compute the separations. Checks on the accuracy of the process were obtained by getting the sums for $J = 8$ from the levels $J = 7$; the exact method for $J = 8$ gives

$$2.688 \text{ (sym)} \quad 0.805 \text{ (anti)} \quad 12.169 \text{ (sym)} \quad 3.506 \text{ (anti)}$$

as the contributions to the state and energy sums respectively (see Table I), while the approximation gives the corresponding values

$$2.667 \text{ (sym)} \quad 0.828 \text{ (anti)}; \quad 12.083 \text{ (sym)} \quad 3.684 \text{ (anti)}.$$

Since the contribution to the energy sum from states with $J > 8$ is only about 5% of the whole sum, and the contribution to the state sum from the same levels is less than 2%, we see that the error introduced into the entropy by the approximation cannot exceed 0.005.

<div align="center">TABLE I</div>

<div align="center">Rotational Entropy of Steam at 300°K</div>

J	State Sum		Energy Sum	
	Sym. Terms	Antisym. Terms	Sym. Terms	Antisym. Terms.
0	3.000	0.000	0.000	0.000
1	7.502	5.095	1.365	0.828
2	27.555	5.947	13.295	3.040
3	23.016	10.602	22.322	9.966
4	27.591	7.072	41.568	10.840
5	15.555	6.431	33.665	13.906
6	11.417	3.190	32.971	9.133
7	5.094	1.982	18.495	7.247
8	2.688	0.805	12.169	3.586
9	1.025	0.355	5.514	1.933
10	0.396	0.129	2.550	0.826
11	0.134	0.045	0.997	0.338
12	0.042	0.014	0.360	0.120
13	0.012	0.004	0.117	0.039
14	0.003	0.001	0.033	0.011
15	0.001	0.000	0.006	0.002
	125.03	41.67	185.43	61.82

$$\Sigma_1 = 166.70 \qquad \Sigma_2 = 247.25$$

$$
\begin{aligned}
S_R &= R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \\
&= 1.9858 \times 247.25/166.70 + 4.5725 \times 2.2219 \\
&= 13.104 \text{ cals./deg.}
\end{aligned}
$$

[1] Kramers and Ittmann: *loc. cit.*

The calculation of the rotational entropy was carried out for 300° and 400°; the former calculation is summarized in Table I. The rotational entropy for 400° exceeds that for 300° by $(3R/2).\ln 4/3$ so that we are justified in using the complete "classical" excitation of the rotational energy to get the rotational entropies at higher temperatures from our values at 300°; the numbers so obtained are entered in the column headed S_R in Table II.

Classical methods,[1] using an "effective" moment of inertia, the Ehrenfest "symmetry number" and an added constant $2R \ln 2$ (which allows for spin), lead to a rotational entropy at 300° only 0.007 greater than the value in Table I; if this agreement is not fortuitous, it suggests that for thermodynamic calculations the older formula should be quite satisfactory for asymmetrical rotators, and that the very laborious calculations sketched above could be avoided.

§3: THE ENTROPY OF SATURATED STEAM AT 300°.

Since the vapour pressure of water at 300° is 26.739/760 atm., the translational entropy of saturated steam at this temperature, including the correction from the equation of state, is 41.278. From Table I, $S_R = 13.104$ and $S_V = 0.008$; hence the entropy of saturated steam at 300° is 54.39.

The heat of formation per mole of liquid water at 298.1° and 1 atm. is 68270 cals.[2] and the free energy of formation, under the same conditions, is 56560 cals. Hence

$$S_{H_2O\,(l)} - S_{H_2} - 1/2\,S_{O_2} = -11710/298.1 = -39.29$$

Since S_{H_2} is here[3] 33.98 and S_{O_2} is[4] 49.03, this gives for 298.1° $S_{H_2O\,(l)} = 19.21$ and for 300°, $S_{H_2O\,(l)} = 19.33$. The latent heat of vaporization[5] at 300° is 2432 joules/gram $= 10470$ cals./mole; hence the molar entropy of saturated steam at 300° is $19.33 + 10470/300 = 54.23$, in satisfactory agreement with our calculated value 54.39.

Had we worked from our spectroscopic entropy value for steam at 300°, using the heat of formation, the latent heat of vaporization, and the spectroscopic entropies of hydrogen and oxygen, we should have arrived at a value for the free energy of formation of liquid water at 298.1° only 50 calories higher than the accepted 56560; this difference is well within the limits of possible error.

For higher temperatures and for 1 atmosphere pressure, the entropy of steam is entered in Table II for reference.

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[1] See, for example, Eucken: Physik. Z., **30**, 818 (1929).
[2] Inter. Crit. Tables, **7**, 258.
[3] Giauque: J. Am. Chem. Soc., **52**, 4816 (1930).
[4] Giauque and Johnston: J. Am. Chem. Soc., **51**, 2300 (1929).
[5] Inter. Crit. Tables, **5**, 138.

TABLE II

Molar Entropy of Steam at 1 Atmosphere

T°K.	S_T (ideal)	S_T (actual)	S_R	S_V	S
400	36.062	36.025	13.959	0.043	50.03
500	37.170	37.152	14.626	0.115	51.89
600	38.075	38.066	15.167	0.222	53.46
700	38.840	38.835	15.626	0.346	54.81
800	39.503	39.501	16.024	0.494	56.02
900	40.088	40.088	16.375	0.657	57.12
1000	40.611	40.611	16.688	0.831	58.13
1100	41.084	41.084	16.972	1.020	59.08
1200	41.516	41.516	17.231	1.215	59.96

§4: THE WATER-GAS EQUILIBRIUM.

In Tables III, IV and V, are tabulated the entropies of hydrogen, carbon monoxide and carbon dioxide for temperatures ranging from 300° to 1200° and for 1 atmosphere pressure. In the case of hydrogen, the rotational-vibrational entropy was calculated by the method of Giauque[1], though a direct calculation in the standard way using a moment of inertia 0.48×10^{-40} and a fundamental frequency $\omega_0 = 4262 - 113.5n$ gives entropy values differing from those obtained by his method by 0.04 at most. For carbon monoxide,[2] the moment of inertia used is 14.9×10^{-40} and $\omega_0 = 2155 - 12.7n$, while for carbon dioxide, the moment of inertia[3] is 70.2×10^{-40} and $\omega_1 = 2295$, $\omega_2 = 672.5$ and $\omega_3 = 1223.5$ cm^{-1} (Eucken's frequencies).[4] In the case of carbon dioxide, alternate rotational levels ($J = 1, 3, \ldots$) are missing, and

TABLE III

Molar Entropy of Hydrogen at 1 Atmosphere

T°K.	S_T	S_{RV}	S
300	28.110	5.894	34.00[5]
400	29.538	6.461	36.00
500	30.646	6.910	37.56
600	31.551	7.279	38.83
700	32.316	7.594	39.91
800	32.979	7.872	40.85
900	33.564	8.123	41.69
1000	34.087	8.354	42.44
1100	34.560	8.572	43.13
1200	34.992	8.778	43.77

[1] See Giauque: J. Am. Chem. Soc., 52, 4817 (1930), Table I.
[2] Mulliken: Phys. Rev., (2) 32, 206 (1928).
[3] Houston and Lewis: Proc. Nat. Acad. Sci., 17, 231 (1931).
[4] Eucken: Z. Physik, 37, 714 (1926).
[5] Giauque's value viz. 33.98 for 298.1° would correspond to 34.02 for 300°; the slight discrepancy arises from our use of R = 1.9858 while he used R = 1.9869.

TABLE IV

Molar Entropy of Carbon Monoxide at 1 Atmosphere

T°K.	S_T	S_R	S_V	S
300	35.948	11.369	0.000	47.32
400	37.376	11.940	0.008	49.32
500	38.484	12.383	0.031	50.90
600	39.389	12.745	0.075	52.21
700	40.154	13.051	0.137	53.34
800	40.817	13.316	0.215	54.35
900	41.402	13.550	0.303	55.26
1000	41.925	13.759	0.397	56.08
1100	42.398	13.948	0.495	56.84
1200	42.830	14.121	0.591	57.54

TABLE V

Molar Entropy of Carbon Dioxide at 1 Atmosphere

T°K.	S_T (ideal gas)	S_T (actual gas)	S_R	S_V	S
300	37.294	37.282	13.072	0.838	51.19
400	38.722	38.715	13.643	1.458	53.82
500	39.830	39.825	14.086	2.224	56.14
600	40.735	40.732	14.448	2.981	58.16
700	41.500	41.498	14.754	3.716	59.97
800	42.163	42.163	15.020	4.414	61.60
900	42.748	42.748	15.253	5.076	63.08
1000	43.271	43.271	15.463	5.702	64.44
1100	43.744	43.744	15.652	6.205	65.69
1200	44.176	44.176	15.825	6.860	66.86

TABLE VI

Molar Heat Capacities in Cals. Deg.$^{-1}$ at Constant Pressure (1 atm.)

T°K.	Steam	Hydrogen	Carbon Monoxide	Carbon Dioxide
300	—	6.91[1]	6.96	8.99
400	8.26	6.96	7.00	9.98
500	8.45	6.97	7.11	10.79
600	8.68	6.99	7.27	11.44
700	8.93	7.03	7.44	11.96
800	9.19	7.08	7.61	12.39
900	9.46	7.13	7.77	12.74
1000	9.74	7.20	7.91	13.04
1100	10.02	7.28	8.03	13.28
1200	10.29	7.38	8.13	13.49

[1] Extrapolated from Giauque: J. Am. Chem. Soc., 52, 4821 (1930).

the frequency ω_2 has the weight $n_2 + 1$; the correction for deviation from ideality was obtained by using a van der Waals equation of state, and amounts to 0.012 at most (see Table V).

The heat capacities of these three gases and of steam were computed by means of the relation $C_P = T(\partial S/\partial T)_P$, and are entered in Table VI.

If Q is the heat of reaction at T° for $CO + H_2O \rightarrow H_2 + CO_2$ and if S_X is the entropy of a constituent X at a partial pressure P_X, then at equilibrium

$$Q = T(S_{CO} + S_{H_2O} - S_{H_2} - S_{CO_2}) \tag{6}$$

Hence, if K stand for $P_{CO}.P_{H_2O}/P_{H_2}.P_{CO_2}$,

$$R \ln K = -Q/T + \Sigma S' \tag{7}$$

where $\Sigma S'$ stands for a quantity identical in all respects with that enclosed in the brackets in Eq. 6 except that all the entropies are now for T° and 1
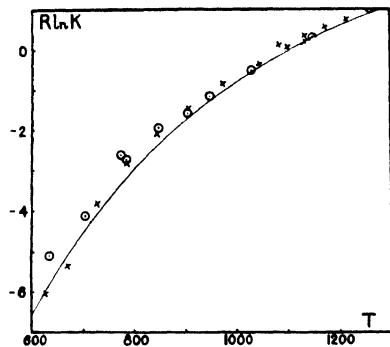
FIG. 1

atmosphere.   In the second line of Table VII values of Q/T are entered for a range of T from 600° to 1200°; they were obtained from Bryant's value[1] of Q for 298°, viz. 9751 cals., by graphical integration of the specific heat curves.   The mean heat capacity of steam between 298° and 373° was taken to be 7.81, which is consistent with the latent heats of vaporization[2] at these two temperatures and with the mean heat capacity of water (18.02) over the same range.   Between 373° and 400° the heat capacity of steam was taken to be 8.23, a value obtained in the same way as the numbers entered in Table VI; the other heat capacities needed for the calculation were taken from that table.   The values of $\Sigma S'$ were obtained from Tables II, III, IV and V, and R ln K (see Table VII) was found by difference; the numbers so found were used to construct the curve in the figure.   The experimental values of Neumann and Köhler[3] are shown for purposes of comparison; their values when approaching equilibrium from the CO, H_2O side are indicated by small circles, and those when approaching equilibrium from the CO_2, H_2 side, are indicated by small crosses.

[1] Bryant: Ind. Eng. Chem., 23, 1019 (1931).

[2] Inter. Crit. Tables, 5, 138.

[3] Neumann and Köhler: Z. Elektrochemie, 34, 218 (1928), Tables 12 and 13.

TABLE VII

The Equilibrium Constant for the Water-Gas Reaction

T°K	600	700	800	900	1000	1100	1200
Q/T	15.30	12.75	10.82	9.33	8.13	7.16	6.36
ΣS′	8.68	8.27	7.92	7.61	7.33	7.10	6.87
R ln K	−6.62	−4.48	−2.90	−1.72	−0.80	−0.06	+0.51

The calculated curve lies in general about 0.2 cals./deg. below the best curve drawn through their points. This difference is within the limit of error of a calculation such as ours, and could be made to disappear by slight adjustments in the moments of inertia; for example, if we had used the conventional 63.5×10^{-40} for carbon dioxide instead of the more recent 70.2×10^{-40}, our calculated curve would have been 0.2 higher throughout.

Our entropy values for 300° (together with Bryant's value for the heat of reaction) lead to a free energy change at 298.1° for the water gas reaction ($-\triangle F°_{298.1}$ in Lewis and Randall's notation) of 6810 calories as compared with Bryant's 6750-6830 calories.

Summary

The entropy of saturated steam for 300° and of superheated steam at 1 atmosphere from 400° to 1200° is calculated, using the rotational levels for an asymmetrical rotator and the spectral constants of Mecke. In conjunction with the calculated entropies of hydrogen, carbon monoxide and carbon dioxide, the equilibrium constant of the water-gas reaction for the range 600°-1200° is then calculated. The divergence of the calculated results from these of experiment is no greater than would be expected to arise from the uncertainties in the data used for the calculation.

The University of Toronto,
Toronto, Canada.
January, 1932.

REMARKS CONCERNING THE CLAUSIUS-MOSSOTTI LAW*

BY PIERRE VAN RYSSELBERGHE

It is well known that the dielectric constant of a dielectric which is *perfect*, *homogeneous* and *isotropic* obeys the Clausius-Mossotti law[1,2,3]:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \text{Constant} = P \tag{1}$$

in which ϵ is the dielectric constant,

     M the molecular weight,

     d the density.

The constant has the dimensions of a volume and is called the molecular polarization. It is defined by the relation

$$P = \frac{4\pi}{3} N\alpha \tag{2}$$

in which N is Avogadro's number and α is the molecular polarizability.

The Clausius-Mossotti law can also be written as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha \tag{3}$$

in which n is the number of molecules per unit volume.

When the Clausius-Mossotti law is written as above, the use of the Gauss C. G. S. system of units (dielectric constant and magnetic permeability of vacuum both equal to unity), or of the electrostatic C. G. S. system of units (dielectric constant of vacuum and velocity of light both equal to unity) is required. The law cannot be used as such in the electromagnetic system of units (magnetic permeability of vacuum and velocity of light both equal to unity) or the practical system of units (unit of length = 19^9 cm., unit of mass = 10^{-11} gm., unit of time = 1 second, magnetic permeability of vacuum and velocity of light both equal to unity). In these two systems of units the numerical value of the dielectric constant of vacuum is $1/900$.

The purpose of this note is to give the Clausius-Mossotti law a form independent of the system of units and to derive it in a general way applicable to all dielectrics which are *perfect, homogeneous* and *isotropic*, including those which are permanently polarized. The derivations of the Clausius-Mossotti law usually given in text-books implicitly suppose that the Gauss C. G. S. or the electrostatic C. G. S. system of units are used and fortuitously give the correct result for permanently polarized dielectrics.

[1] O. F. Mossotti: Mem. di mathem. e fisica in Modena, **24** II, 49 (1850).

[2] R. Clausius: "Die mechanische Wärmetheorie," **2**, 62 (1879).

[3] P. Debye: "Polare Molekeln," 7 (1929).

A *perfect, homogeneous* and *isotropic* dielectric is a dielectric for which the polarization vector $\bar{I}$ is given by

$$\bar{I} = \bar{I}_0 + k\,\bar{\bar{H}} \tag{4}$$

$\bar{I}_0$ being the polarization corresponding to a total electrostatic field zero,
$\bar{H}$ being the total electrostatic field,
k being the electric susceptibility
and for which k is independent of $\bar{H}$ and of the coordinates.[4] The electrostatic induction $\bar{B}$ is given by:

$$\bar{B} = \epsilon_0\bar{H} + 4\pi\bar{I} \tag{5}$$

in which ϵ_0 is the dielectric constant of vacuum.
The vector

$$\bar{R} = \bar{H} + \frac{4\pi}{3\epsilon_0}\,\bar{I} \tag{6}$$

is the total force acting on a punctual charge of unity when the volume of a spherical alveolus dug around the charge tends towards zero. It is called the "electric resultant."[5]
Debye's "inner field" $\bar{F}$[6] is related to R by:

$$\bar{F} = \epsilon_0\bar{R} \tag{7}$$

We see that $\bar{R}$ has the dimensions of an electrostatic field $(\epsilon_0^{-1/2}L^{-1/2}M^{1/2}T^{-1})$ while $\bar{F}$ has the dimensions of an electrostatic induction $(\epsilon_0^{+1/2}L^{-1/2}M^{1/2}T^{-1})$. Applying equation (4) we deduce from (5) and (6):

$$B = \epsilon\bar{H} + 4\pi\bar{I}_0 \tag{8}$$

$$\bar{R} = \frac{\epsilon + 2\epsilon_0}{3\epsilon_0}\bar{H} + \frac{4\pi}{3\epsilon_0}\,\bar{I}_0 \tag{9}$$

with

$$\epsilon = \epsilon_0 + 4\pi k \tag{10}$$

ϵ is the dielectric constant of the dielectric. We see that

$$\frac{B}{H} = \epsilon + 4\pi\frac{I_0}{H} \tag{11}$$

when $\bar{I}_0$ and $\bar{H}$ are parallel.
Let us write:

$$\bar{I} = n\alpha\epsilon_0\left(\bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I}\right) + \left(1 - \frac{4\pi n\alpha}{3}\right)\bar{I}_0 \tag{12}$$

which is equivalent to:

$$\bar{I} = n\alpha\bar{F} + \left(1 - \frac{4\pi n\alpha}{3}\right)\bar{I}_0 \tag{13}$$

in which n is the number of molecules per unit volume and α the molecular polarizability.

[4] Th. De Donder: "Théorie mathématique de l'électricité," 90 (1925).
[5] Th. De Donder: loc. cit., p. 79.
[6] P. Debye: loc. cit., p. 6.

From (12) we deduce:

$$\bar{I} = \frac{n\alpha\epsilon_0}{1 - \dfrac{4\pi n\alpha}{3}}\bar{H} + \bar{I}_0 \qquad (14)$$

Comparing this relation with (4) we see that:

$$k = \frac{n\alpha\epsilon_0}{1 - \dfrac{4\pi n\alpha}{3}} \qquad (15)$$

Introducing the value of I as given by (14) into (5) we find:

$$\bar{B} = \epsilon_0\bar{H} + \frac{4\pi n\alpha\epsilon_0}{1 - \dfrac{4\pi n\alpha}{3}}\bar{H} + 4\pi\bar{I}_0 \qquad (16)$$

while equation (8) gives

$$\bar{B} = \epsilon\bar{H} + 4\pi\bar{I}_0 \qquad (17)$$

From (16) and (17) we deduce:

$$\frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} = \frac{4\pi n\alpha}{3} \qquad (18)$$

and

$$\frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} \cdot \frac{M}{d} = \frac{4\pi N\alpha}{3} \qquad (19)$$

which is the general form of the Clausius-Mossotti law. If instead of (12) we write:

$$\bar{I} = n\alpha\epsilon_0\left(\bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I}\right) \qquad (20)$$

(16) becomes:

$$\bar{B} = \epsilon_0\bar{H} + \frac{4\pi n\alpha\epsilon_0}{1 - \dfrac{4\pi n\alpha}{3}} = (\epsilon_0 + 4\pi k)\bar{H} = \epsilon\bar{H} \qquad (21)$$

and the correct Clausius-Mossotti formula could be deduced from this equation. (20) and (21) are however both wrong because $\bar{B}$ is not equal to $\epsilon\bar{H}$ when $\bar{I}_0$ is different from zero. A correct reasoning would be to start by differentiating (5), (8) and (12). One has then:

$$d\bar{B} = \epsilon_0 d\bar{H} + 4\pi d\bar{I} \qquad (22)$$

$$d\bar{B} = \epsilon d\bar{H} \qquad (23)$$

$$d\bar{I} = n\alpha\epsilon_0\left(d\bar{H} + \frac{4\pi}{3\epsilon_0}d\bar{I}\right) \qquad (24)$$

Replacing $d\bar{I}$ in (22) by its value deduced from (24) and equating the two expressions of $d\bar{B}$ one obtains again the Clausius-Mossotti formula. The dielectric constant is defined by equation (23), the constant of integration being $4\pi\bar{I}_o$, as shown by (17).

If $\bar{I}_o = o$ the dielectric is said to be *soft*. We have in this case:

$$\epsilon = \frac{dB}{dH} = \frac{B}{H} \tag{25}$$

Summary

A general expression of the Clausius-Mossotti law, independent of the system of units and valid for all dielectrics which are perfect, homogeneous and isotropic has been established.

Stanford University,
California.

AN IMPROVED COMMUTATOR AND SOME SOURCES OF ERROR IN THE COMMUTATOR METHOD FOR THE MEASUREMENT OF OVERVOLTAGE*

BY A. L. FERGUSON AND G. M. CHEN[1]

Two methods have been extensively used for the measurement of overvoltage commonly known as the direct and commutator methods. Investigators have found that invariably the direct method gives values higher than the commutator method. For more than forty years an explanation has been sought for these observations; and during this time hundreds of researches have been carried out. The explanation offered may be classified into two groups. According to one the discrepancy is due to the existence of a resistance that is different from the ordinary electrolytic resistance between the electrode and the adjacent electrolyte. This resistance has been given various names such as surface resistance, contact resistance, film resistance, transfer resistance, etc. According to the other group the interrupter, which is a necessary part of the equipment for the commutator method, does not permit the measurement of the total discharge potential because of the rapid drop in potential during the interval between the interruption of the current and the measurement of the potential. The question is one of great importance because the values obtained by the two methods in many instances have been found to differ by a large amount and no complete theory of overvoltage, passivity or valve action can be formulated as long as this situation exists.

Several years ago a thorough investigation of this subject was started in this laboratory and has been in progress intermittently since that time. In the first article[2] it was shown beyond any doubt that practically all data obtained with a commutator by previous investigators were open to serious criticism. It was proven that the commutator gives values that are averages over the whole charge or discharge interval. This means that such commutators could never give, directly, values as high as those obtained by the direct method, and offered a possible explanation for the discrepancies between the two methods.

In the second paper[3] an attempt was made to show that the value at the beginning of the discharge interval is the same as at the end of the charge interval; in which case there would be no reason to postulate the existence of transfer resistance. The data all pointed strongly in that direction but the design of the commutator was such that values could not be obtained within 4° of the end of the charge interval, and about 4° of the beginning of

[2] Trans. Am. Electrochem. Soc., 45, 311 (1924).

[3] Trans. Am. Electrochem. Soc., 47, 227 (1925).

the discharge interval.   The potential was changing so rapidly, particularly on discharge, that it was not safe to extrapolate through these ranges.   There were grounds to suspect, also, that the brushes introduced some uncertainties, particularly when the commutator was used at more than one speed.

Before the present work was started the commutator was completely rebuilt with different design to eliminate the difficulties that had been discovered.   A new system for the manipulation of the brushes also was employed, which made it possible to explore the region much nearer the end of charge and beginning of discharge than could be done with the old interrupter. In the previous work it was necessary to change the speed of the commutator, which was shown to be a serious disadvantage.   By the new arrangement it was not necessary to stop the commutator or change its speed during a complete series of measurements.
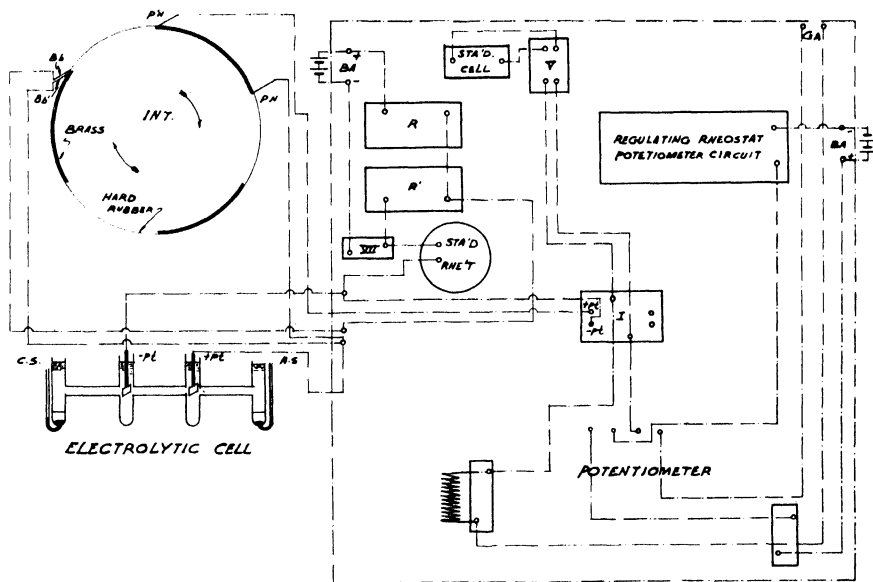
Fig. 1

The essential parts of a potentiometer-commutator assembly for the measurement of decomposition potentials.

Apparatus

The most essential parts of the set-up are shown in Fig. 1.   The desired potential, which is obtained as an I.R. drop over resistance R', may be applied to the cell through the charging brushes (Bb and Bb'), represented in contact with a brass section of the interrupter (Int).   The potentiometer is connected to the anode and cathode of the cell through the brushes P_n and P_n' represented in contact with another brass segment near the ends.

The commutator consists of two interrupters directly connected to a $\frac{1}{2}$ horse power motor (see Fig. 2).   Each interrupter is made of a disk of hard rubber 2.8 cm. wide and 20 cm. in diameter.   The edge is divided into 360°
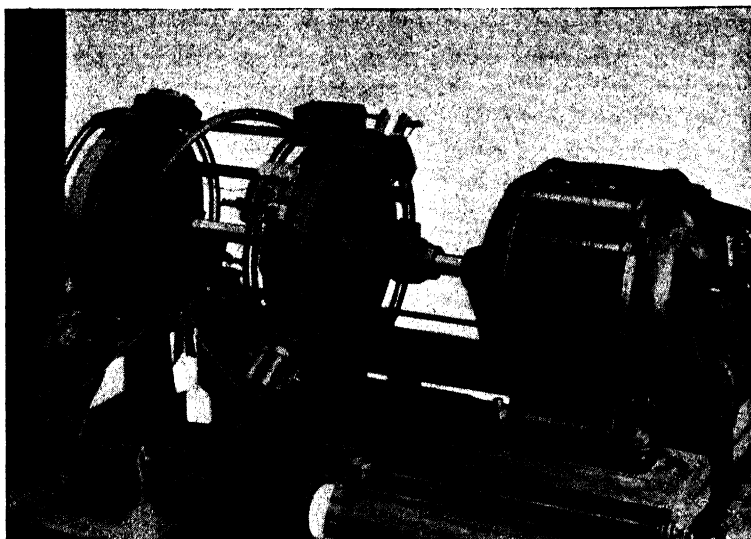
FIG. 2

A direct driven two-disk commutator.
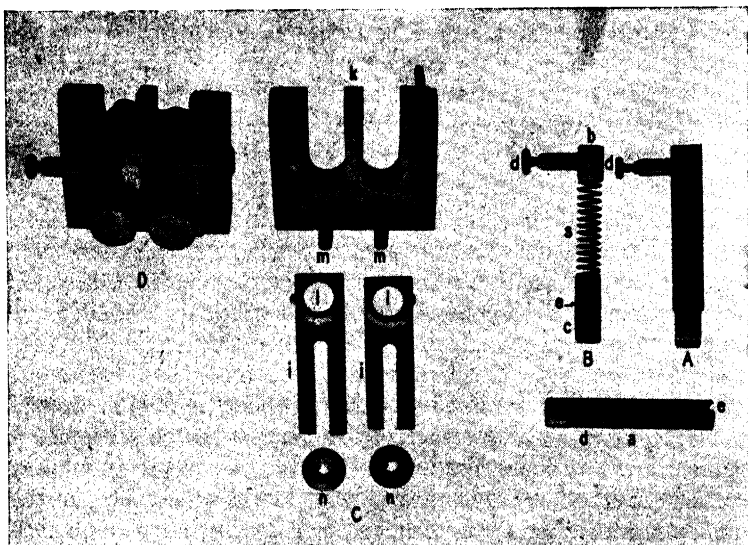
FIG. 3

Brush and brush holder assemblies.

by a scale.   In the surface three brass sections each 60° long are set 60°
apart, and separated by three hard rubber sections of equal length.   The
surfaces of the disks are wide enough so that two brushes may be mounted
in parallel and thus make contact with the brass segments at the same time.
The disks may be shifted to any position on the shaft.

The various parts and the construction of the brushes and brush holders
are represented in Fig. 3.   The complete brush and holder assembly is shown
in (A), and the various parts in (B).   The brush proper is made of solid copper
of a shape indicated by (c).   This is soldered to a spring (S) the other end of
which is soldered to a piece of brass (b).   The holder (a) is a piece of brass
tubing with two narrow openings (d) and (e).   The assembly consisting of
brush (c), spring (S) and brass piece (b) all slipped inside the holder (a) and
held in place by the binding post (d) which passes through opening (d) on
the holder.   There is a small projection (e) on the brush that fits into the
opening (e) and keeps the brush in the proper position.   By means of the
spring, and the binding post operating in slot (d) the tension of the brush
on the interrupter can be changed.

Surrounding each disk of the commutator is an arrangement for support-
ing the brushes in position (see Fig. 2).   Some of the details of a brush sup-
port are shown in (C) and (D) of Fig. 3; the various parts are shown in (C)
and the assembly in (D).   It consists of two parts, the brass strip (i) and the
hard rubber support (k).   The brass strip has a neck (l) at one end through
which the brush assembly (A) may pass; at the other end is a deep slot
which enables the brush to be adjusted to any position in the slot of the hard
rubber support (k) and held in place by the bolt (m) and nut (n) as illustrated
in (D).   This whole assembly may be mounted in any position on the frame
surrounding the disks as shown in Fig. 2.

The electrolytic cell system is represented diagrammatically in Fig. 1.
Two-normal sulfuric acid was used throughout.   The reference electrodes
were mercurous sulfate and the electrodes in the decomposition cell were
platinized platinum.

Experimental

Many experiments were carried out to study such conditions as current
density, speed of interrupter, kind of brushes, tension of brushes, length of
time commutator was operated, presence of dissolved gases, position of tip
of reference electrode, etc.   Only a few typical sets of data are recorded,
however, in this report.

Table I shows the influence of current density.   The time in column (1)
is given in seconds from the beginning of the charge or discharge interval.
The potentials of the anode against the anode standard are given in column
(2); cathode against cathode standard in column (3); the total applied
potential minus the I.R. drop through the solution, or, in other words, the
sum of (2) and (3) in column (4), the total discharge potential in column (5);
and the difference between the total charge potential at the end of charge
and the beginning of discharge in column (6).   In all experiments conditions
were the same except current density and this was made greater in each
succeeding experiment.

TABLE I

Comparison of Charge and Discharge Potentials at Different Current Densities

Platinized platinum electrodes. Time is given in sec. after beginning of charge or discharge. The applied potential is greater for each succeeding experiment.

(1) Time $\times 10^{-4}$	(2) Pt.$^+$—A.S. (charge)	(3) Pt.$^-$—C.S. (charge)	(4) Pt.$^+$+Pt.$^-$ (3) + (2)	(5) Pt.$^+$—Pt.$^-$ (discharge)	(6) End of charge minus beginning of discharge
Experiment (1) Average C.D. = .0006 amp./cm²					
24	1.126	0.716	1.842	1.855	0.000
end	1.138	0.717	1.855	1.841	
Experiment (2) Average C.D. = .0016 amp./cm²					
17	1.210	0.726	1.936	1.954	0.000
end	1.228	0.726	1.954	1.936	
Experiment (3) Average C.D. = .0021 amp./cm²					
11	1.222	0.732	1.954	1.979	0.001
end	1.248	0.732	1.980	1.954	
Experiment (4) Average C.D. = .028 amp./cm²					
14	1.312	0.758	2.070	2.059	0.069
end	1.369	0.759	2.128	1.984	

The data in column (6) show that at high current densities there is still an appreciable difference between the values for the end of charge and the beginning of discharge. The fact that the agreement is good at low but not at high current densities supports the idea that there is a contact resistance at the interface between electrodes and solution as many investigators have contended. Such a resistance would use up some of the measured charge potential before it reached the electrode. More information on this point is furnished by the data in Table II.

If the differences observed in Table I are due to surface resistances these should be appreciably different at the two electrodes. To test this point the charge and discharge potentials were measured separately for each electrode at a series of current densities. The data are recorded in Table II. Column (2) gives the anode charge potential at the end of charge; column (3), at the beginning of discharge; and column (4) the difference between (3) and (2). Columns (6), (7) and (8) give similar data for the cathode. It should be observed that the differences increase with current density as in Table I. If the differences are due to I.R. drops then the resistances may be obtained by dividing the values in columns (4) and (8) by the corresponding currents. The values thus obtained are recorded in columns (5) and (9).

TABLE II

Anode and Cathode Potentials on Charge and Discharge

(1) Time × 10⁻⁴	(2) Pt.+ − A.S. (End of charge)	(3) Pt.+ − A.S. (Dis-charge)	(4) Pot. diff.	(5) Resis-tance	(6) Pt.− − C.S. (End of charge)	(7) Pt.− − C.S. (Dis-charge)	(8) Pot. diff.	(9) Resis-tance
Experiment (1) current 0.0024								
0		1.106	0			0.698	0	
9		1.105				0.698		
578		1.098				0.698		
609	1.106				0.698			
Experiment (2) current 0.0086								
0		1.190	0.004	.5		0.732	0.004	.5
8		1.187				0.731		
578		1.157				0.724		
609	1.194				0.736			
Experiment (3) current 0.0143								
0		1.234	0.016	1.1		0.734	0.011	.8
9		1.230				0.733		
660		1.178				0.731		
708	1.250				0.745			
Experiment (4) current 0.0265								
0		1.270	0.027	1.0		0.743	0.010	.8
7		1.265				0.741		
506		1.198				0.736		
543	1.297				0.762			
Experiment (5) current 0.0365								
0		1.283	0.043	1.2		0.745	0.031	.9
8		1.279				0.743		
565		1.193				0.737		
649	1.326				0.776			
Experiment (6) current 0.046								
0		1.295	0.054	1.2		0.744	0.042	.9
9		1.289				0.742		
660		1.196				0.734		
708	1.349				0.786			
Experiment (7) current 0.054								
0		1.316	0.061	1.1		0.747	0.052	.9
8		1.305				0.745		
565		1.203				0.736		
649	1.377				0.799			

The surprising fact is the resistances are practically the same for each electrode and do not change with current density and are, therefore, not due to transfer resistances. In fact it was shown later that the resistances were due to the combined resistances of the electrodes and lead wires of the charging circuit between the electrodes and the points where the potentiometer circuit made contact. In all later work the leads were reduced in length as much as possible and when necessary corrections were made.

To study the nature of the resistance of the commutator brushes an arrangement represented in Fig. 4 was used. The two sets of brushes a and a′ and b and b′ were set 60° apart and in parallel position on the interrupter. The brushes a and b, also, a′ and b′ were connected through the switch I. The potential divider R′ was used as the source of current which passed through the ammeter and either the set of brushes b and b′ or a and a′ depending upon which was in contact with a brass segment. The voltmeter measured the fall of potential over whichever pair of brushes was carrying the current. The voltmeter reading divided by the ammeter reading gave the resistance in the brush contacts.
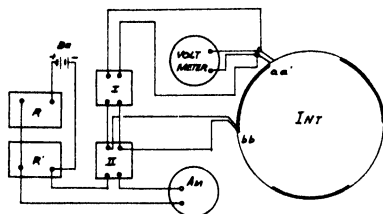
FIG. 4
Diagram of the arrangement for producing a continuous direct current through the brushes of a rotating commutator.

Measurements were taken with three different current densities and various r.p.m.s. and are represented in Fig. 5. The curve shows that the resistance of the commutator brushes increases with increase of r.p.m. but is independent of current density. The results are surprisingly reproducible as shown by the agreement of the three sets of data.

Since, in the commutator method, the current passes through the brushes on the interrupter, an I.R. drop at the contact is inevitable. This drop is very small at low, but is considerable at high current densities, particularly at high commutator speeds. As a result, the applied potential that actually reaches the electrodes from a common source varies with these factors. In other words, the potential from a common source that actually reaches the electrodes is different in the commutator method and the direct method. This subject was studied more fully with an arrangement similar to Fig 4, which permitted the applied potential to be measured in three ways.

The data are recorded in Table III. The first column indicates the method used. In the *direct method* (a) a direct continuous potential was applied to the cell without passing through the interrupter; in the *commutated direct method* (b) a direct continuous potential was applied through the interrupter by two sets of brushes arranged as indicated in Fig. 4; in the *commutator method* (c) a direct intermittent potential was applied through the interrupter which is the regular commutator arrangement; and in the *"direct method"* (d) the system was the same as (a) except a resistance equal to the
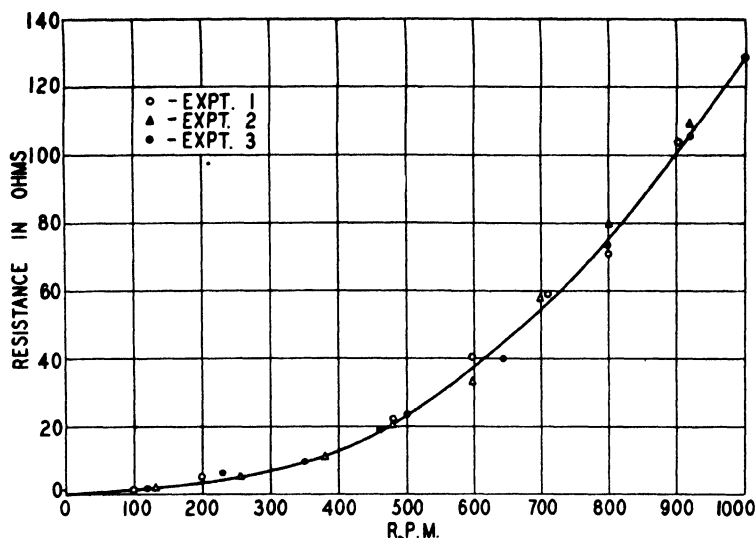
FIG. 5
Curve showing change of brush contact resistance with speed of rotation of commutator.

TABLE III

Comparison of Four Methods for measuring Polarisation

(1) Method	(2) R − R′	(3) Pt.⁺ − Pt.⁻ (Charge)	(4) Pt.⁺ − A.S. (Charge)	(5) Pt.⁻ − C.S. (Charge)	(6) (4) + (5) / Pt.⁺ − Pt.⁻	(7) Pt.⁺ − Pt.⁻	(8) I (Amp.)
Experiment (1)							
(a)	2.037	2.000	1.145	0.734	1.879		0.00338
(b)	2.043	1.995	1.145	0.734	1.879		0.00320
(c)	2.018	1.937	1.121	0.729	1.850	1.850	0.00350
(d)	2.042	1.995	1.145	0.734	0.870		0.00320
Experiment (2)							
(a)	2.322	2.229	1.232	0.750	1.982		0.00844
(b)	2.345	2.200	1.229	0.748	1.977		0.00740
(c)	2.233	2.011	1.210	0.738	1.948	1.943	0.00804
(d)	2.347	2.205	1.230	0.748	1.978		0.00740
Experiment (3)							
(a)	2.498	2.345	1.265	0.757	2.022		0.0136
(b)	2.518	2.298	1.228	0.757	1.985		0.0126
(c)	2.520	2.283	1.219	0.750	1.969	1.946	0.0131
(d)	2.517	2.298	1.226	0.756	1.982		0.0126
Experiment (4)							
(a)	3.084	2.770	1.312	0.768	2.080		0.0273
(b)	3.177	2.789	1.312	0.765	2.077		0.0240
(c)	3.120	2.665	1.289	0.749	2.038	2.015	0.0249
(d)	3.161	2.789	1.312	0.764	2.076		0.0240

brush resistance determined in (b) was inserted in series with the electrolytic cell. The measurements were taken by all four methods at the same time with the same ratio of resistances R'/R of the potential divider used as the source potential. The magnitude of the source potential is given in column (2). In the various experiments all conditions were held constant except the ratio of resistances in the potential divider, and this was changed so as to give a higher source potential for each succeeding experiment.

A comparison of the results in rows (b) and (d) for the various experiments shows that for all measurements made by the commutated direct method (b) and "direct method" (d) the data obtained are practically the same. This indicates that passing the charging current through the resistance of the commutator brushes is equivalent to passing it through a constant carbon resistance. A comparison of the data in rows (a) and (b) shows that in all cases the current (column 8) and also the polarisation (columns 3, 4, 5 and 6) are greater in the direct method (a) than in the commutated direct method (b). This is due to the fact that in the latter the brush resistance is included in the circuit and prevents the total source potential from reaching the electrodes. It may be observed, further, from the data in rows (a), (c) and (b) (column 2) that the source potentials in the former two are less than in the latter though the ratio of resistances on the potential divider is the same. The variation of this common source potential is undoubtedly caused by the change of the apparent resistance of the potential divider as the result of the addition, in the parallel circuit, of the resistance of the commutator brushes in the commutated direct method and by the change of e.m.f. of the cell in these two methods. The resistance of the commutator brushes is of course equal to zero in the direct method.

An inspection of the data in rows (c) (column 8) shows that the current is higher than in (b) and (d) but lower than in (a). It is lower than in (a) because of the added resistance of the brushes and it is higher than in (b) and (d) because it is an intermittent current while in (b) and (d) the current is continuous. An intermittent current of the same value as a continuous one produces less average polarisation. This conclusion is borne out by the observed data recorded in columns 6, 7, and 8 as pointed out above.

These data show that any resistance which develops at the brushes will cause an increase in source potential at the potential divider but will at the same time diminish the charging current; which means that, in a comparison of the direct and commutator methods for measuring overvoltage, the experimenter may apply a certain potential to the cell by the direct method and obtain a certain polarisation potential, then he may apply supposedly this same potential through a commutator and expect that he should get the same polarisation, and in case he does not, he may conclude that the two methods do not give the same value. The data in Table III show that he is not justified in this assumption but rather should expect a lower polarisation, as he actually finds, in the latter case because of the lower current which the data show is always obtained. It is advisable, therefore, in a comparison of the two methods to use a low speed of rotation of the commutator in order to

minimize the resistance of the commutator brushes. It should be pointed out, also, that commutator data obtained at definite intervals of charge or discharge, to be used for extrapolation purposes, must be obtained at the same r.p.m., a point that has not been given sufficient consideration in the past.

Some investigators have contended that in a comparison of the two methods the current densities employed in the two methods should be the same. The data in Table III, columns 6 and 8, show that this conclusion is not true. The current by the commutator method is in all cases slightly higher than by the methods (b) and (d), yet the polarisation is in all cases less. If the current were made equal in the two cases then the difference in polarisation would be even greater, which means that it is not to be expected that the polarisation should be the same by the two methods at the same current density. The reason for this is evident; in the commutator method the current flows intermittently and thus produces less polarisation, or to put it differently, during the time the intermittent current is not flowing the polarisation decreases a little.

Summary

1. A commutator is described which makes it possible to measure charge or discharge potentials within 0.0003 sec. from the beginning or end of the charge and discharge intervals for the electrodes either combined or separately.

2. Several sources of error that may enter into the measurements of polarisation potentials by the commutator method have been pointed out.

THE MEASUREMENT OF POLARISATION BY THE DIRECT AND COMMUTATOR METHODS*

BY A. L. FERGUSON AND G. M. CHEN[1]

In the previous article the authors have described a new commutator which possesses several desirable features and eliminates some of the undesirable features found in other commutators. Some important sources of error, also, were pointed out.
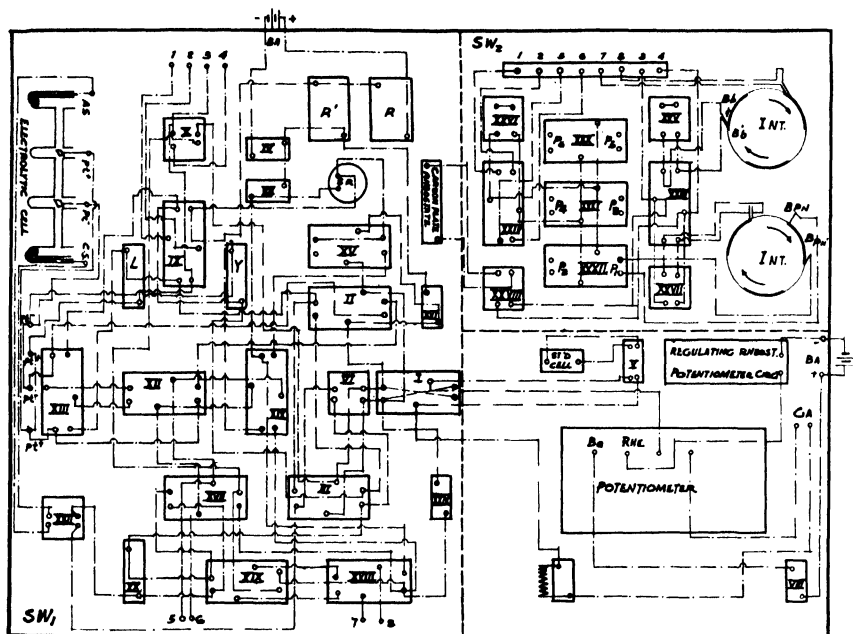
FIG. 1
Complete wiring diagram of switch-board used in polarisation measurements.

In the present work it was found advisable to introduce several additions to the set-up in order to measure the potential over every part of the circuit, even including the lead wires; the object being to make certain that all potentials were correctly measured and that there was no potential or I.R. drop in any part of the circuit unaccounted for. By this arrangement the sum of all the separate potentials in the whole circuit could be checked with the source potentials.

The final system is represented in Fig. 1. A summary of the manipulation of the switches necessary for the more important measurements is given in Table I. To make a measurement, the switches listed following that measurement should be closed and all others opened.

TABLE I

A. Charge potential with the interrupter rotating.

Switches XXIII and XXIV closed down and P_n closed

(P_n indicates the P_1, P_2, P_3, etc. required)

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^+$ − A.S.	I, III (left), XII (left), XIII (down), XXII.
Pt.$^-$ − C.S.	I, III (right), XII (left), XIII (up), XXII, XX.
A.S. − C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XIV (up).
S.R.	I, XV (right), XIV (up).
Box Pot.	I, XVI, XIV (down), XXIX.

B. Discharge potentials with interrupter rotating.

Switches XXIII and XXIV closed up and P_n closed

Potential to be measured	Switches to be closed
Discharge	I, II (left), II (down), r.
Pt.$^+$ − A.S.	I, III (left), IX (down), XXII.
Pt.$^-$ − C.S.	I, III (right), II (up), XX, XXII.

C. Direct method.

Switches XXIII closed up, XXV and XXVI closed

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^+$ − A.S.	I, III (left), XII (left), XIII (down).
Pt.$^-$ − C.S.	I, III (right), XII (left), XIII (up).
A.S. − C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XVII (right), XXIX.
S.R.	I, XIV (up), XV (right).
Box Pot.	I, XIV (down), XVI, XXIX.

Symbols used for various potentials:

Pt.$^+$ − A.S. = anode potential vs anode standard.
Pt.$^-$ − C.S. = cathode potential vs cathode standard.
Pt.$^+$ − C.S. = anode potential vs cathode standard.
Pt.$^-$ − A.S. = cathode potential vs anode standard.
Pt.$^+$ + Pt.$^-$ = sum of the single electrode potential of anode and that of cathode.
Pt.$^+$ − Pt.$^-$ (charge) = potential, anode vs cathode, including the I.R. drop through the solution.
Pt.$^+$ − Pt.$^-$ (discharge) = potential, anode vs cathode, equal to the sum of electrode potentials on discharge.
C.D. = current density.
Box Pot. = common source of potential taken from the potential divider.
Hg.$^+$ − Hg.$^-$ or I.R. = I.R. drops through the solution, or potential between two reference electrodes.
Br. = potential across the brushes.
S.R. = potential across the standard resistance.

The electrolytic cell system was changed somewhat from that used before. The new arrangement is shown in Fig. 2. This more complex system was designed to prevent the diffusion of mercurous ions into the decomposition cell from the reference electrodes, and to eliminate any I.R. drop between the electrode of the decomposition cell and the reference electrode. Two normal sulfuric acid was used in all experiments. In some experiments the electrodes were platinized and in others bright.

The heart of the whole equipment is, of course, the commutator. For a description see the previous paper. An end view of one of the interrupters giving considerable detail is shown in Fig. 3.
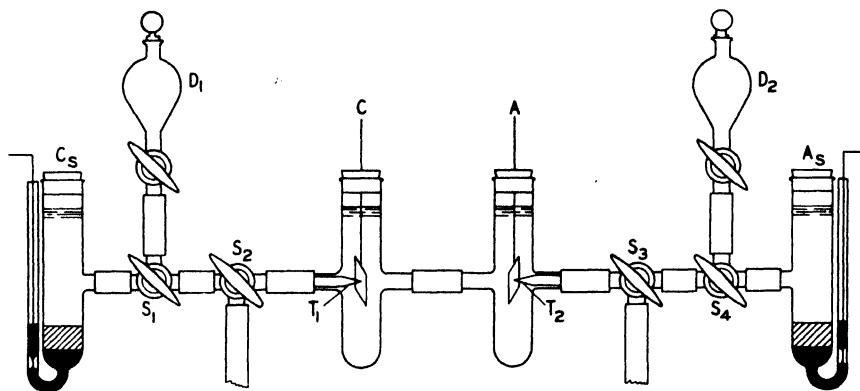
FIG. 2
Cell system for polarisation measurements.

The charging brushes B_b, are set in parallel so that both make contact at the same instant. The potentiometer brushes B_{p1} and $B_{p1'}$ are set $59°$ apart which means they close the potentiometer circuit during only one degree once every $1/3$ of a revolution. The potential measured is, then, the average during a time interval equal to $lx(1/360) \times (60/r.p.m.)$ sec. If the interrupter rotates clockwise and has come to the position shown in Fig. 3, the charging brushes have made contact on a brass plate for one degree and during this same time the potentiometer brushes B_{p1} and $B_{p1'}$ have made connection to the potentiometer through switch P_1 in S_{w2} of Fig. 1. The potential measured is the average value of the potentials during only this one first degree of charge, since, after the interrupter has turned more than one degree the connection to the potentiometer is broken at B_{p1}. After 7 degrees, connection is made again for a period of one degree by brushes B_{p2} and $B_{p2'}$. In a similar manner other pairs of brushes are used to measure either charge or discharge or both after any desired known intervals of time at constant r.p.m. and practically simultaneously.

If the potentiometer contact be made for one degree and the potentiometer brushes commence to make connection after the charging brushes have been in contact with the brass section of the interrupter for "d" degrees, then the

time interval after charge starts corresponding to the potential measured is
d − ½ degrees or in seconds is given by the expression

$$(d - \tfrac{1}{2})\ (1/350 \times 60/\text{r.p.m.})$$

One might think, at first, that with the apparatus here described it should
be possible to reduce the discharge time interval to any desired value by in-
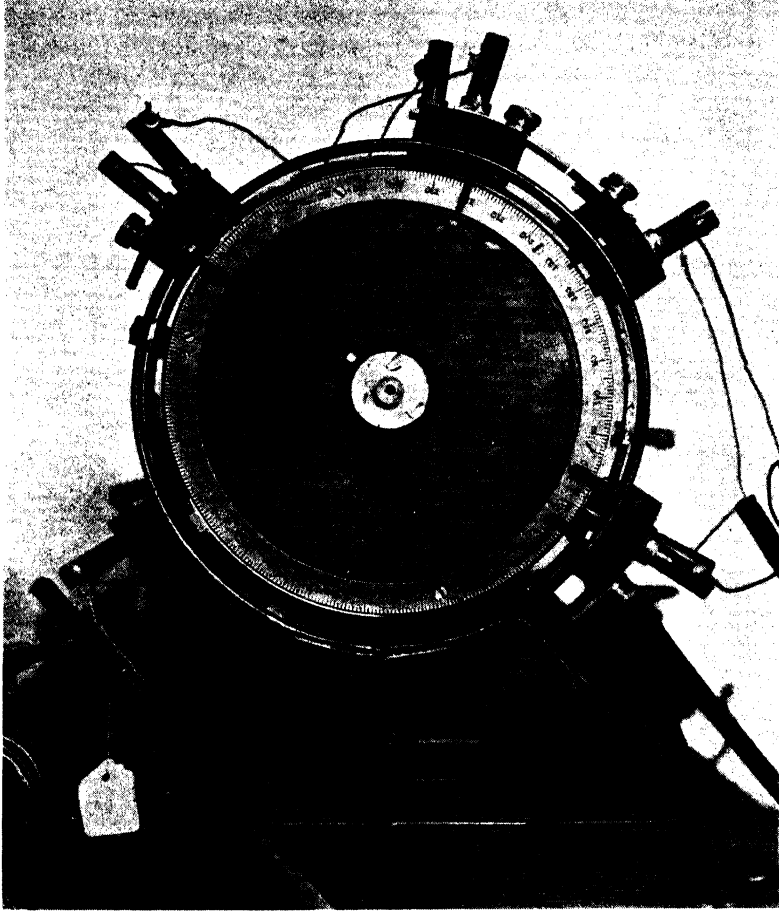
FIG. 3
End view of one disk of commutator.

creasing the speed of the interrupter. From the formula it is evident the time
interval may be changed by decreasing or increasing the R.P.M. Several
factors enter in, however, which place a limit upon the time-interval and still
obtain reliable data. In the first place, as will be shown later, sufficient time
must be allowed for the charge to reach a maximum during each charge
interval. In the second place, the discharge potential at the instant the
current is interrupted cannot be measured because the charging brushes

must have completely left the brass section of the interrupter before the potentiometer contact is made. This interval amounts to about 0.0001 second at 400 R.P.M. for the brushes used; and they are as thin (1 mm.) as other conditions will permit. In the third place, in order that the potentials shall be measured accurately to one millivolt the potentiometer circuit must be closed at least 0.0005 second. If, now, the electrode potential at the beginning of discharge is determined as soon as the apparatus will permit after the interruption of the current at the R.P.M. 400 and at a time interval just necessary for the potentiometer contact, the time during which the average potential is obtained is .0006 second. By assuming the average potential to be the actual potential at a time equal to half of the total interval, the shortest possible discharge interval at which potential can be measured is 0.0003 seconds after discharge has begun. These limitations are imposed by the very nature of equipment required in the commutator potentiometer method.

Among the advantages of the equipment used in this work not possessed by those previously used may be listed the following: (1) measurements may be made by both the direct and commutator methods at the same time; (2) both charging and discharging potentials may be measured at different and known intervals of charge and discharge without stopping the interrupter; (3) potentials can be determined as near the end of charge and beginning of discharge as the physical limitations inherent in the potentiometer commutator method will permit; (4) Anode, cathode and total potentials can be measured practically at the same time; (5) The I.R. drop between the electrodes may be measured directly; (6) Every individual potential throughout the charging circuit may be measured and their sum compared with the total potential delivered to the system; (7) Only one speed of the interrupter is required for a complete set of measurements.

Experimental

Hundreds of measurements were made with this outfit which were highly reproducible and satisfactory; but only a few typical sets are included in this report.

It was stated that the charge potential requires some time to reach a maximum value and that in a comparison of the direct and commutator methods care must be taken to see that sufficient time is allowed for the maximum to be reached. This is clearly evident from the curves of Fig. 4, where charge and discharge potentials are plotted against time from the beginning of the charge interval. Curves (a) and (a') are the charge and discharge curves for a current density of 9 m.a., and (b) and (b') for 90 m.a. For each set of curves the current density was held constant, also, the speed of rotation of the interrupter. Each point was determined by a separate set of brushes. Readings were taken in rapid succession and then repeated as a check. It was found advisable in all cases to pass a continuous direct current through the cell for at least half an hour before starting the interrupter. Measurements were not taken until the intermittent current had

been flowing about five minutes. These curves make clearly evident the following points. (1) It is possible, by means of the interrupter used, to obtain definite values for any part of either the charge or discharge interval and thus to plot a complete cycle. (2) The rate of charge and discharge at the various portions of the charge and discharge intervals depends upon the current density and is much greater at the start the higher the current density. (3) The time required to reach maximum charge is greater the lower the current density. (4) The only way to be certain the charge potential has reached its maximum value is to determine the charge curve.

The curves in Fig. 5 show the relation between current and cell potential as both change with time. The current increases much more rapidly than the potential and reaches a maximum after which it shows a slight but characteristic decrease as the potential increases.
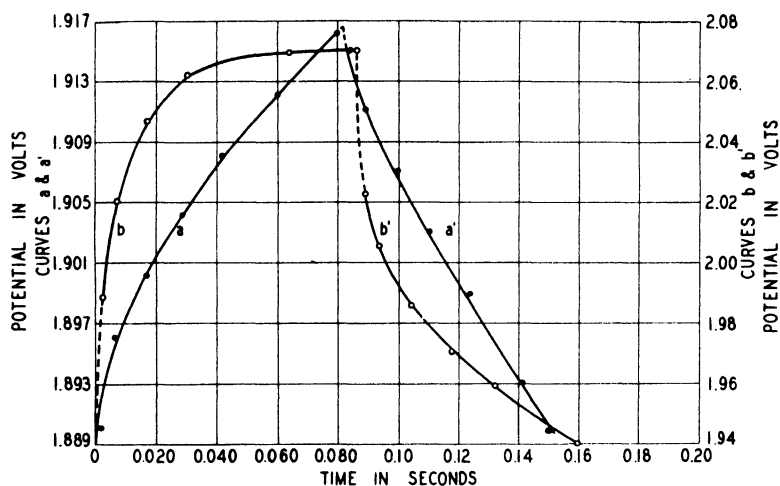
FIG. 4

Charge and discharge curves by commutator potentiometer method.

Attention was concentrated especially upon the portions of the curves at the end of charge and beginning of discharge as these are the parts which are of greatest interest and the portion which the redesigned commutator made it possible to study. The work reported earlier indicated that if measurements could be made close enough to the end of charge and the beginning of discharge the values would be found equal and thus proof furnished that there is no such thing as transfer or any other kind of surface resistance.

A typical set of data is given in Table II. The time in seconds recorded in column (1) corresponds to the interval after discharge has begun. Only one value for charge is recorded and that is for the time corresponding to 59° and is considered that at the end of charge since the charge had reached a maximum.

The average current density was determined by measuring the I.R. drop over a standard resistance during the total charge interval. Columns (3) and (7) contain the single electrode potentials at the end of charge minus the I.R.

drop through the connecting wires. The resistance of the electrode and connecting wire to the point where the potential was determined was in these experiments 0.24 ohms. The electrode potential values in columns (4) and (8), at zero time of discharge were obtained by extrapolation from the discharging curves. In each of the eight experiments, conditions were maintained constant except the current density which was made higher in each succeeding experiment. As the current density increases from 3.8 m.a. to 149 m.a.
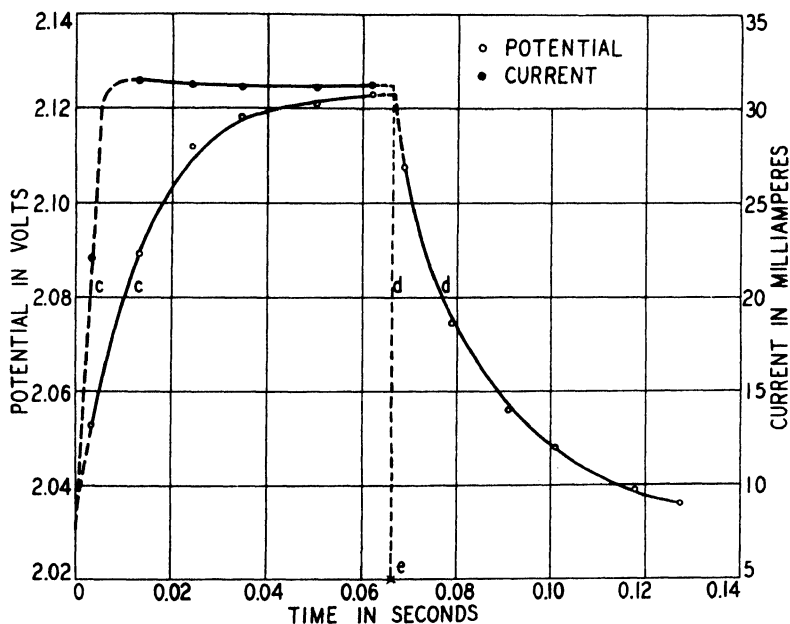
FIG. 5

Current and potential charge and discharge curves.

the polarisation of the cathode increases only 24 m.v. but the anode increases 282 m.v. The cathode drops two or three millivolts during the first few thousandths of a second then remains constant during the remainder of the discharge interval. The anode potential drops much more rapidly and continues to drop throughout the whole discharge interval. The anode potentials for some of the experiments are represented as curves in Fig. 6. The ends of the charge curves are represented as horizontal dotted lines since the potential had reached a constant maximum value. It should be noticed that the first point on the discharge curves was taken about 0.0008 sec. after the beginning of the discharge interval and the greatest extrapolation was only 9 m.v. The differences in potentials between the end of charge and zero time of discharge are given in columns (5) and (9). They amount to about 2 m.v. which is practically within the limits of experimental or extrapolation errors. This is the first time that anything like so close agreement has been found for such high current densities.

TABLE II

Relation between single electrode potentials on charge and on discharge at various current densities. Platinized electrodes. Time is in Sec. $\times$ 10⁴.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Pt.⁺ − A.S.		Pt.⁺ − A.S.		Pt.⁻ − C.S.		Pt.⁻ − C.S.	
Time × 10⁴	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.

Experiment (1) Average C.D. = 0.0038

0			1.040	− 1			0.707	0
8			1.039				0.706	
40			1.038				0.705	
140			1.036				0.705	
460			1.032				0.705	
550			1.031				0.705	
590	1.039	1.039			0.707	0.707		

Experiment (2) Average C.D. = 0.0178

0			1.165	0			0.722	− 1
8			1.164				0.721	
40			1.162				0.719	
140			1.153				0.719	
460			1.138				0.719	
550			1.131				0.719	
590	1.167	1.165			0.723	0.721		

Experiment (3) Average C.D. = 0.0284

0			1.210	− 1			0.725	− 2
8			1.209				0.724	
40			1.204				0.722	
140			1.193				0.722	
460			1.167				0.722	
550			1.161				0.722	
590	1.212	1.209			0.726	0.723		

Experiment (4) Average C.D. = 0.0436

0			1.254	− 1			0.728	− 1
8			1.252				0.727	
40			1.246				0.725	
140	.		1.225				0.725	
460			1.197				0.725	
550			1.193				0.725	
590	1.259	1.253			0.723	0.727		

<div align="center">TABLE II (continued)</div>

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Pt.+−A.S.		Pt.+−A.S.		Pt.−−C.S.		Pt.−−C.S.	
Time ×10⁴	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.

Experiment (5) Average C.D. = 0.0722

0			1.272	−2			0.729	−1
7			1.268				0.728	
33			1.256				0.726	
129			1.231				0.726	
423			1.200				0.726	
506			1.193				0.726	
543	1.278	1.270			0.736	0.728		

Experiment (6) Average C.D. = 0.0936

0			1.290	−2			0.729	−2
8			1.286				0.728	
40			1.272				0.726	
140			1.249				0.726	
460			1.210				0.726	
550			1.204				0.726	
590	1.299	1.288			0.738	0.727		

Experiment (7) Average C.D. = 0.1228

0			1.296	+2			0.730	0
7			1.290				0.729	
32			1.277				0.727	
122			1.250				0.727	
400			1.210				0.727	
479			1.201				0.727	
513	1.313	1.298			0.745	0.730		

Experiment (8) Average C.D. = 0.1490

0			1.322	+2			0.731	+1
7			1.313				0.730	
33			1.293				0.729	
129			1.264				0.729	
423			1.220				0.729	
506			1.214				0.729	
543	1.342	1.324			0.750	0.732		

These data confirm the prediction made in an earlier paper that the potential at the beginning of charge and the end of discharge would be found equal if reliable measurements could be made. This means that transfer resistance or any other kind of resistance is not present at the surface of electrodes for the system just described.
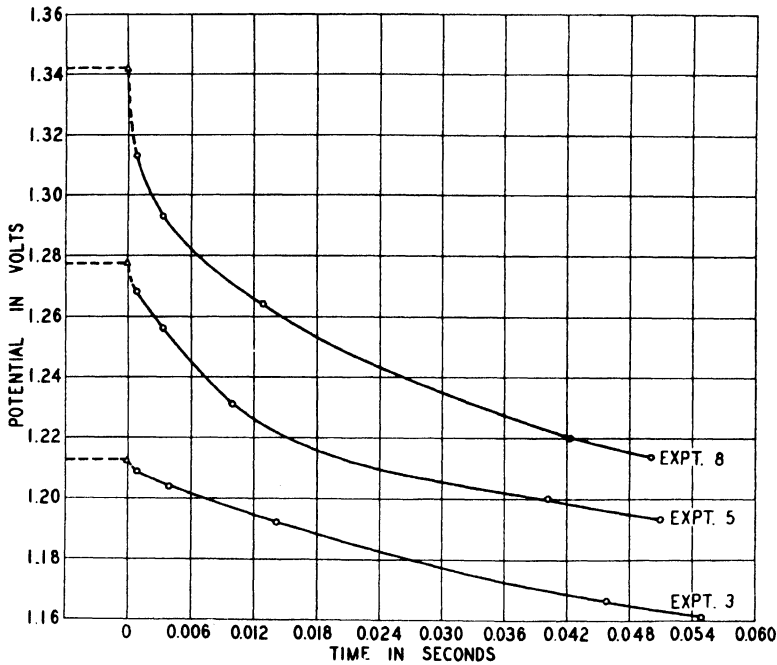
FIG. 6

Anode discharge curves for platinized electrodes.
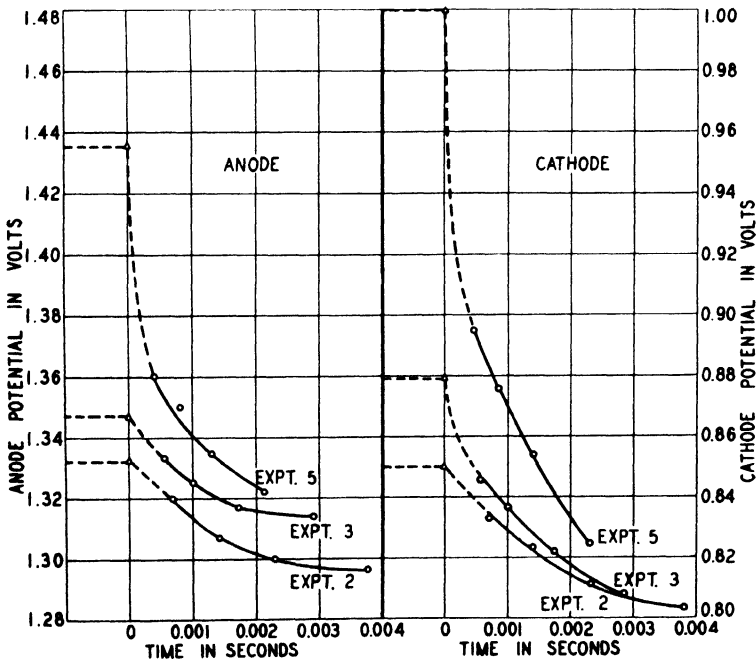
FIG. 7

Anode and cathode discharge curves for bright platinum electrodes.

TABLE III

Relation between single electrode potentials on charge and on discharge at various current densities. Smooth platinum electrode.

(1) Time × 10^-4	(2) Pt.+ – A.S. End of charge	(3) Pot. corr.	(4) Pt.+ – A.S. Discharge	(5) Pot. diff. m.v.	(6) Pt.– – C.S. End of charge	(7) Pot. corr.	(8) Pt.– – C.S. Discharge	(9) Pot. diff. m.v.

Experiment (1) R.P.M. = 210, Average C.D. = 0.0001

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0			1.183	0			0.689	1
8			1.182				0.688	
15			1.181				0.688	
24			1.181				0.688	
40			1.181				0.687	
470	1.183	1.183			0.690	0.690		

Experiment (2) R.P.M. = 220, Average C.D. = 0.0016

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0			1.333	1			0.850?	0?
7			1.320				0.833	
14			1.307				0.824	
23			1.300				0.811	
38			1.296				0.803	
443	1.332	1.332			0.850	0.850		

Experiment (3) R.P.M. = 290, Average C.D. = 0.0026

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0			1.347?	0?			0.862?	17?
5.7			1.333				0.846	
10			1.325				0.837	
17			1.317				0.822	
29			1.314				0.807	
336	1.347	1.347			0.879	0.879		

Experiment (4) R.P.M. = 400, Average C.D. = 0.0360

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0			1.366?	20?			0.892?	24?
4			1.355				0.855	
8			1.344				0.833	
13			1.335				0.821	
21			1.325				0.811	
248	1.390	1.386			0.920	0.916		

Experiment (5) R.P.M. = 360, Average C.D. = 0.0500

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
0			1.380?	49?			0.920?	74?
4.6			1.360				0.895	
8.3			1.350				0.876	
14			1.335				0.854	
23			1.322				0.825	
271	1.435	1.429			1.000	0.994		

Measurements were next carried out with smooth platinum electrodes. The data are recorded in Table III, and some are represented as curves in Fig. 7. A comparison of the data in Table III with those in Table II shows some pronounced differences. This is especially noticeable for the cathodes. While the platinized cathode increased in potential only 24 m.v. for a change in current density from 3.8 m.a. to 149 m.a., the smooth platinum changed about 200 m.v. for a current density change from 0.1 m.a. to only 50 m.a. The smooth platinum anode, on the other hand showed a considerably smaller change with current density than the platinized anode. The rate of decrease in potential on discharge was much greater for both anode and cathode with smooth than with platinized platinum, and here again the rate of decrease was much greater for the cathode than for the anode. At extremely low current densities smooth and platinized electrodes for both electrodes do not show these abnormal effects. It is clearly evident from the curves that, even though the first points on the discharge curves were obtained only about 0.0004 sec. after discharge started the potential had dropped probably 50 to 75 m.v. This is much too great a rate of change for safe extrapolation to zero time. This means that the commutator potentiometer method can not be relied upon to give satisfactory results for smooth platinum electrodes.

Summary

1. A commutator was used which enabled potentials to be measured within 0.0005 sec. from end of charge or beginning of discharge.

2. The system permitted the measurement of every potential drop in the complete circuit, and their sum could be compared with the source potential.

3. Measurements were made for anode, cathode and total potentials at several points on the charge and discharge intervals, practically simultaneously, without stopping the interrupter, so that curves could be plotted for complete cycles.

4. It was proven that for platinized electrodes in two-normal sulfuric acid there is no surface resistance of any kind for current densities between 3.8 and 150 m.a.

5. With smooth platinum electrodes the decrease in discharge potential is so rapid that satisfactory results can not be obtained with the interrupter potentiometer system.

DETERMINATION OF ADHESION TENSION OF LIQUIDS AGAINST SOLIDS. A MICROSCOPIC METHOD FOR THE MEASUREMENT OF INTERFACIAL CONTACT ANGLES[1]

BY F. E. BARTELL[2] AND E. J. MERRILL[3]

The primary purpose of the present investigation was to obtain evidence concerning the validity of certain assumptions made in the development of the method of Bartell and Osterhof[4] for the determination of adhesion tension of solids against liquids. It was desired to obtain an independent check on the contact angle values and the corresponding adhesion tension values as determined by them. In their work contact angles were determined indirectly by a pressure of displacement method; in the work described herein, contact angles were measured directly by a microscopic method.

In this paper only a brief review of the pressure of displacement method can be included. Over a century ago Thomas Young[5] pointed out that a simple relationship existed between the different interfacial tension values of interfaces in contact and the resultant angle of contact formed by their intersection, and proposed that the following relation should hold,

$$S_1 - S_{12} = S_2 \cos \theta_{12} \qquad (1)$$

S_1 = the surface tension of the solid.

S_2 = the surface tension of the organic liquid.

S_{13} = the interfacial tension of water against the solid.

S_{23} = the interfacial tension of water against organic liquid.

A_{12} = the adhesion tension of an organic liquid against a solid.

A_{13} = the adhesion tension of the water against the solid.

θ_{12} = the liquid-air-solid contact angle.

θ_{23} = the interfacial contact angle between liquid-liquid interface and the solid.

Freundlich[1] more recently suggested that the adhesion tension of a liquid against a solid (A_{12}) should be given by the expression,

$$A_{12} = S_1 - S_{12} = S_2 \cos \theta_{12} \qquad (2)$$

If the contact angle formed by a liquid-air-solid system were greater than a zero angle, then with equation (2) the adhesion tension value for the liquid against solid could be determined by measuring the surface tension of the liquid and the angle of contact. In a few instances this procedure is possible, but with nearly all liquids the contact angle is zero and hence the adhesion tension values become indeterminate. To overcome this difficulty, Bartell and Osterhof made use of the following formulation:

$$A_{13} - A_{12} = S_{12} - S_{13} = S_{23} \cos \theta_{23} \qquad (3)$$

With the A_{12} value determined for a single liquid by equation (2), it was possible, by obtaining the interfacial tension of liquid against liquid, S_{23}, and the interfacial contact angle, θ_{23}, to determine the adhesion tension of water, A_{13}, according to equation (3). When once the adhesion tension of water was thus determined, the adhesion tension of other (organic) liquids against the solid could be found by using the same equation and again determining the interfacial tensions and the contact angles of these other water-organic liquid-solid systems.

In order to measure contact angles, Bartell and Osterhof used an apparatus consisting of a cell with an inlet tube at one end and an attached manometer at the other. In one half of the cell was packed water-wet solid while in the other half, the organic liquid-wet solid. When powdered silica was used as the solid material, the water tended to displace the organic liquid from the powder and in so doing set up a pressure which was read with a manometer. Assuming that the pores of the powder served as a multiple capillary system, and assuming that an equilibrium contact angle was formed in each of the pores, they calculated the value of this contact angle by the formulation,

$$\cos \theta_{23} = gPr/2 \, S_{23},$$

in which g = gravitational constant.

      P = manometer pressure in gms/cm².

      r = average effective radius of all capillaries.

In accepting measurements of this nature it is evident that three fundamental assumptions were made:

(1) That the fine pore structure of the solid is equivalent to a large cluster of single capillary tubes.

(2) That within each system a state of equilibrium is finally reached which includes in effect an equilibrium contact angle in each pore.

(3) That the formulations of Young and of Freundlich, and likewise their own derivations from these, are sound and hence give valid results.

It is the substantiation of all three of these hypotheses that this paper primarily undertakes.

[1] "Colloid and Capillary Chemistry," 157 (1926).

The Photomicrographic Method

Casual microscopic observations of liquid-air-solid menisci and of liquid-liquid-solid interfaces set up in small capillary tubes suggested that true representations of these might be secured by means of a photomicrographic apparatus. Then if it could be shown that such interfaces, when located in small capillaries, are either hemispherical or sectors of spheres, or that the variance therefrom is so small as to lie within the range of other experimental errors, it should be possible to project these photographic images upon the screen under large magnification and to make a fairly accurate measurement of the contact angles. Transparent capillary tubes were made available by using transparent quartz. This material was desirable since much of adhesion tension data obtained in this laboratory had been procured with silica.

Experimental Method and Apparatus

Satisfactory capillary tubes with diameters ranging from 0.2 mm. to 0.6 mm. were drawn from larger sized transparent quartz tubing. Only those were accepted for use which were found to have a uniform cylindrical bore. At first attempts were made to clean the tubes after drawing them. After much experimentation it was found that the washing of the inside walls of the tubes with acids produced undesirable changes on these surfaces and hence the practice thereafter was to use tubes just as taken from the fire in the drawing process. Glass capillaries were prepared for use in the same manner.

The method of studying the curvature and the contact angle was that of obtaining the photomicrograph of the liquid interface or meniscus upon a photographic plate which could be used as a lantern slide. With this negative, projections were then made upon a screen of white paper.

The photomicrographic apparatus consisted of an arc lamp, condensers, filters, heat absorption cell, adjustable light shutter, an immersion cell with constant temperature control for the capillary tubes, a microscope, an attached camera and a projection lantern.

Perhaps the greatest difficulty encountered in the work was that of overcoming the effect due to the different indices of refractions of the various parts of the different systems. This applied to the tube material, the liquid contained within, and the air or second liquid. It will be evident that the simplest system to study would be one composed of a liquid, air and a solid of which the liquid and the solid have the same index of refraction. An example of this kind is that of carbon tetrachloride-air-silica. By using an immersion liquid in the immersion cell which also had the same index of refraction as the silica, there would come through the microscope to the photographic plate a true image of the meniscus and of the contact angle.

To determine whether the curvature of the menisci, in the size of capillaries that were to be used, were actually constant, a number of liquids possessing the same index of refraction as the material of the capillary walls were first studied. Figs. 1-8 inclusive show photographs of the menisci of

such liquids. It is apparent that the contact angles formed in the first four cases are greater than zero, and that those in the last four are zero or at least nearly so. Careful measurement showed them to be zero angles. By the aid of the projection lantern and a pair of dividers, a large number of such menisci were studied upon the screen at magnifications of 1000 diameters or greater. In no case could the slightest deviation from a constant curvature be found when the photographs had been accurately made with correct illumination. The need of the latter must be duly recognized. A small air bubble trapped within the liquid of one of the above systems serves as a desirable means of checking this factor. Illumination must be adjusted so as to give the circular outline of the bubble in the center of the tube image.

That the curvatures are constant is further substantiated by the fact that when angle values were later calculated upon the basis of this assumption, duplicate values for the same liquid in different tubes could be obtained even though the diameters of the tubes differed by as much as 300 percent. The work of Richards and Carver[1] also tends to check this conclusion.

Accepting the premise that the curvature of such menisci are constant, the

FIG. 1   FIG. 2   FIG. 3   FIG. 4   FIG 5   FIG. 6   FIG. 7   FIG. 8

method for measuring the value of the contact angle is shown in Fig. 9. ACB represents a cross section of the meniscus of the system, AB is the diameter of the tube and OB the radius of curvature. PQ is drawn tangent to the curve at point B. The angle of contact, θ, will then be equal to the angle θ', and the measurement of the latter will give the value sought. When the contact angle is greater than zero the points A and B are readily located as shown. If the angle is of zero value, the radius of curvature and the radius of the tube will be identical.

Not all liquids have the same index of refraction as that of the material of the capillary wall. With such liquids the meniscus will appear distorted, Fig. 10, and a need of some modification of the previous method might at first thought appear to be demanded. The premise of the constant curvature of the meniscus will, however, still stand, for there is no reason for believing that the refractive index of a liquid will in any way affect the meniscus curvature. Furthermore, it is apparent that the point C on the meniscus, Fig. 11, will appear in its true position regardless of refractive index, since the light from this point will pass directly through the liquid and on through the wall
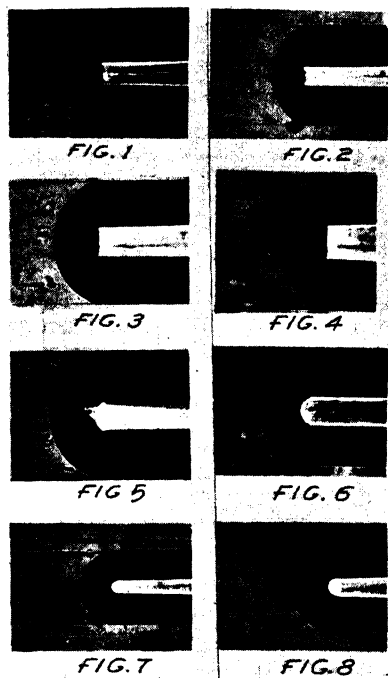
[1] Richards and Carver: J. Am. Chem. Soc., **43**, 827 (1921).

of the tube without deflection.   Observations will further show that, in spite
of the differing indices of refraction of the liquid and the wall of the tube, the
true positions of A and B are clearly indicated, due to the difference in light
dispersion produced by the liquid and the air at the line of intersection.   And
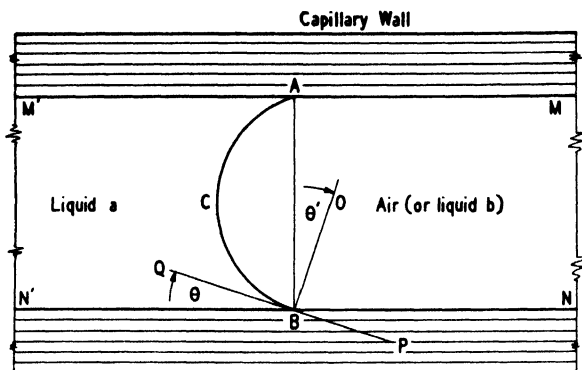
FIG. 9

Contact Angle. Liquid (or liquids) with index of refraction same as that of capillary wall.

so, while the meniscus will appear to be, in such cases as these, either in some
position as A'CB' or as A''CB'', the true positions of A, C, and B will still
establish the true curvature and thus serve as the basis for measuring the
true contact angle.   The method is in effect the same as was used in the
previous case.
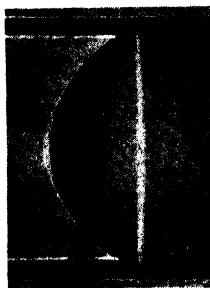
FIG. 10
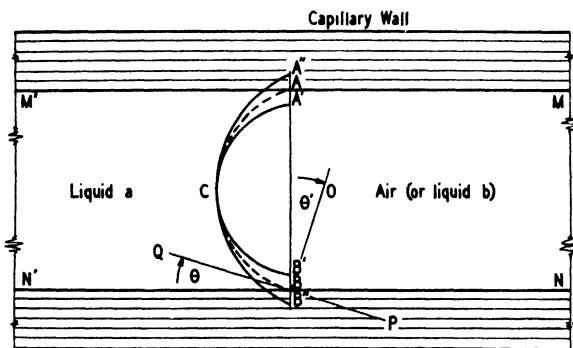
FIG. 11

Contact Angle. Liquid (or liquids) with index of re-
fraction different from that of capillary wall.

Liquid-liquid-solid Systems.—In bringing the surfaces of two liquids to-
gether in a capillary tube for the measurement of the interfacial contact
angle, a small amount of the organic liquid was first allowed to rise in the end
of the tube.   Water was then permitted to displace the organic liquid so
that the water-organic liquid interface was carried to some convenient
position in the capillary.   The water end of the tube was then quickly sealed.
The capillary was then kept at a constant temperature.

In a manner identical with that used to determine the type of curvature of the meniscus of the liquid-air-solid systems, liquid-liquid-solid interfaces were likewise found to possess constant curvatures. In determining this, pairs of immiscible liquids, each having the same index of refraction as the capillary wall material, were brought together and a study made as before. Figs. 12 and 13 show photomicrographs of two such interfaces. For liquids having different indices of refraction the discussion given above applies. The method used for measuring the interfacial contact angle was identical with that of the liquid-air-solid systems.
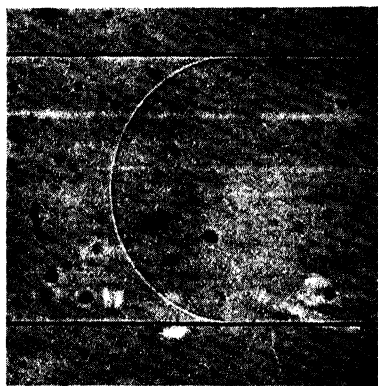
FIG. 12

FIG. 13

The values of some liquid-air-solid and of liquid-liquid-solid contact angles as formed in capillaries of silica and of different glasses are given in Tables I and II.

Equilibrium Contact Angles

Much discussion is to be found in the literature relative to the formation of equilibrium contact angles between liquids and solids. Rayleigh[1] appears to have been one of the first to note the presence of the so-called advancing and receding contact angles. His work was confirmed by that of Miss Pockels.[2] Sulman[3] concluded that "when a liquid reaches its final state of equilibrium by spreading over the dry surface of a solid, the contact angle is greater than when the liquid reaches its final state of equilibrium by receding from a previously wetted surface." He calls this the "hysteresis" of the contact angle, suggesting that the difference in the two angles is due to a changing surface tension of the solid once it is wet by the liquid. This view is shared by Bosanquet and Hartley.[4] Adams and Jessup[5] choose to consider this phenomenon as caused by friction of the liquid and the solid. Thus

[1] Rayleigh: Phil. Mag., 30, 397 (1890).
[2] Pockels: Physik. Z., 15, 39 (1914).
[3] Sulman: Trans. Inst. Min. Met., (1920).
[4] Bosanquet and Hartley: Phil. Mag., 42, 456 (1921).
[5] Adams and Jessup: J. Chem. Soc., 127, 1863 (1925).

additional energy is expended in order to overcome friction as the liquid moves out over the solid surface. Still others[1] conclude that the energy of adsorption of the liquid by the solid constitutes the determining factor.

TABLE I

Liquid-Air-Solid Contact Angles

Liquid	Silica	Pyrex	Lead Glass	Soda-lime Glass
Acetylene tetrabromide	28° 00′	30° 30′	22° 30′	21° 15′
Alphabromnaphthalene	21° 00′	20° 30′	6° 45′	5° 00′
Methylene iodide	33° 00′	29° 30′	30° 00′	29° 00′
Tribromhydrin	20° 15′	—	15° 30′	17° 00′
Alphachlornaphthalene	15° 00′	—	13° 30′	10° 30′
Iodobenzene	12° 10′	—	12° 15′	0° 15′
Bromoform	24° 30′	—	13° 00′	16°
Turpentine	0°	0°	0°	0°
Acetic acid	0°	0°	0°	0°
Glycerine	0°	0°	0°	0°
Carbon-tetrachloride	0°	0°	0°	0°
Xylene	0°	0°	0°	0°
Olive oil	20° 00′	21° 45′		
Oleic acid	27° 00′	27° 30′		

TABLE II

Liquid-Liquid-Solid Contact Angles
(Water—Organic Liquid-Solid)

Liquid	Silica	Lead glass	Soda-lime Glass
Acetylene tetrabromide	30° 30′	34° 15′	0°
Alphabromnaphthalene	33° 00′	37° 30′	0°
Methylene iodide	33° 30′	—	0°
Tribromhydrin	25° 15′	29° 30′	0°
Alphachlornaphthalene	25° 00′	30° 00′	0°
Iodobenzene	25° 30′	—	0°
Bromoform	24° 30′	22° 15′	0°
Benzene	28° 40′		
Toluene	35° 00′		
Carbon tetrachloride	25° 15′		
Hexane (synthetic)	25° 30′		
Nitrobenzene	42° 30′		
Carbon disulfide	42° 30′		
Amyl alcohol	55° 30′		
Butyl acetate	45° 00′		

[1] Ablett: Phil. Mag., **46**, 244 (1923); Rideal: "Surface Chemistry" (1926).

A rigorous treatment of the subject of advancing, receding and equilibrium contact angles has been the subject of another investigation in this laboratory and so will not be further touched upon in this paper; suffice it to say that it now appears that where systems are contained in such small-sized capillary tubes as were used in this investigation, the forces of surface and interfacial tension appear to overcome any distorting effects due to gravity and should quickly bring a meniscus or interface to an equilibrium position and thereby establish an equilibrium contact angle. In this work it was not possible to bring two liquid surfaces together in a capillary tube at precisely such points as will later prove to be the true equilibrium contact points. Hence it is to be expected that some time must elapse before equilibrium will occur; usually from 10 to 24 hours is sufficient. Table III includes two series of readings

TABLE III

Advancing and Receding Contact Angles
Time required to reach equilibrium values
System 1. Water-benzene-silica

| | Value of angle | |
Time of standing	First tube	Second tube
1 hr.	15° 00′	30° 30′
6 hrs.	23° 15′	—
10 ″	—	28° 50′
1 day	28° 45′	28° 20′
2 days	28° 00′	—
3 ″	28° 30′	28° 40′
4 ″	28° 40′	—

for contact angle values as they were measured over consecutive periods of time in two different water-benzene-silica systems. It will be observed that even though the first readings were greater or were less than those of the values finally obtained, both systems eventually gave angles of the same value. These readings are typical of those for all systems studied. Furthermore, the consistent duplication of contact angle values for the same liquids in different tubes which were set up at different times and therefore under somewhat different conditions, makes but one conclusion possible; namely, that although the angle formed before equilibrium conditions are reached may vary and may be either smaller or larger than the final angle, in due time a definite and constant angle will be formed. This latter angle we designate as the equilibrium contact angle. The evidence appears to be conclusive that with both liquid-air-solid and with liquid-liquid-solid systems in single capillary tubes a definite and reproducible contact angle is formed.

Preferential Adsorption

The equilibrium positions taken by the menisci of the liquid-air-solid systems were found to remain always the same no matter how long they were allowed to stand. On the other hand many of the liquid-liquid-solid

interfaces after weeks, or perhaps not until after months, of standing were observed to change and finally to form zero contact angles. A close study of these changing systems showed that water droplets were forming between the organic liquid surface and the wall of the capillary. These drops increased both in number and in size as time went on and then eventually all coalesced into one continuous film of water which completely surrounded the organic liquid column. Such a condition is nearly reached in the system as shown in the photograph of Fig. 14. It seems probable that as the two liquids stood in contact with each other they became mutually saturated. Since the silica has a greater attraction for water than for the organic liquid, the water was preferentially adsorbed by the silica, thus displacing the organic liquid. A slight change in temperature may have induced the initial drop formation and thereby caused the appearance of the water phase at the surface. Further adsorption and drop, or film formation, produces a growth of the film until it becomes continuous. When this happens the contact angle must necessarily become zero.
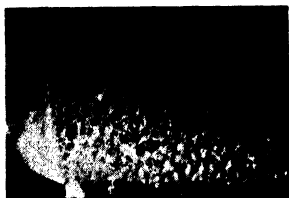
FIG. 14

The above behavior raises the question: have true equilibrium angles really been formed when admittedly the angle may eventually undergo change? Strictly speaking, the angle is not an equilibrium angle, otherwise it would not change. The change is probably due to an alteration in nature of the contiguous phases. The surface of the solid phase becomes altered, it passes from essentially a surface of pure solid to a surface of water, which phase finally covers the solid phase. The preferential adsorption of the water by the capillary wall material is a matter quite secondary to the original condition which gave the apparent equilibrium angle. This latter angle is probably in fact the characteristic angle for the phases in contact at the moment. Although considerable time may be required to obtain this angle, it will remain at a constant value for a comparatively long time. It is believed that this angle can be used to give fairly accurate values for adhesion tension. Further, it should be pointed out that interfacial contact angles measured by the microscopic method have shown good agreement with the interfacial angles obtained by the Bartell-Osterhof displacement pressure method.

Adhesion Tension Values from Contact Angles

It has been previously pointed out that a fundamental value in the determination of the adhesion tension of most organic liquids is the adhesion tension of water itself. To obtain this, it is necessary first to find some liquid or liquids which give a finite contact angle with air and the solid. Table IV gives such liquid-air-solid contact angle values, together with the adhesion tension values for the six liquids used. Table V gives the adhesion tension value of water for silica as determined independently using each of

these different liquids. The close agreement of the six values thus found for water is of much significance. Not only does it give a multiple check on the adhesion tension value for water against silica, but it goes far in checking the validity of the method used, together with all formulations which lie back of it. Similar data for these liquids and lead glass are also given in Tables VI and VII. Table VIII shows the contact angle and adhesion tension values for the organic liquids and soda-lime glass. The adhesion tension of water against this glass cannot be determined since all interfacial contact angles involved are of zero value.

TABLE IV
Liquid-Air-Silica Contact Angles, θ_{12}
Adhesion tension values, liquid-silica, A_{12}

Organic Liquid	θ_{12}	$S_2{}^*$	A_{12}
Acetylene tetrabromide	28° 00′	49.07	43.32
Tribromhydrin	20° 15′	44.76	42.00
α-Br-naphthalene	21° 00′	44.00	41.07
α-Cl-naphthalene	15° 00′	41.20	39.77
Iodobenzene	12° 10′	39.10	38.22
Bromoform	24° 30′	40.93	37.25

TABLE V
Interfacial Contact Angles, θ_{23}
Adhesion tension of water-silica, A_{13}

Organic Liquid	θ_{23}	A_{12}	$S_{23}{}^*$	A_{13}
Acetylene tetrabromide	30° 30′	43.32	38.32	76.34
Tribromhydrin	25° 15′	42.00	38.00	76.37
α-Br-naphthalene	33° 00′	41.07	41.57	75.93
α-Cl-naphthalene	25° 00′	39.77	40.24	76.24
Iodobenzene	25° 30′	38.22	41.34	75.53
Bromoform	19° 30′	37.25	40.35	75.28

Average value of $A_{13} = 75.92$

*All surface tension and interfacial tension values found in the data of this paper are those from the "Critical Tables" corrected to 25°C. In some instances temperature coefficient values were not available and values which appeared to represent justifiable approximations were used. Any errors thus introduced are surely not greater than the experimental errors of our method.

TABLE VI
Liquid-Air-Lead Glass Contact Angles, θ_{12}
Adhesion tension values, liquid-lead glass, A_{12}

Organic liquid	θ_{12}	S_2	A_{12}
Methylene iodide	30° 00′	50.16	43.73
Tribromhydrin	15° 30′	44.76	43.13
α-Br-naphthalene	6° 45′	44.00	43.61
α-Cl-naphthalene	13° 30′	41.20	40.05
Iodobenzene	12° 15′	39.10	38.70
Bromoform	13° 00′	40.93	39.86

TABLE VII

Interfacial Contact Angles, θ_{23}
Adhesion tension values of water-lead glass, A_{13}

Organic liquid	θ_{23}	A_{12}	S_{23}	A_{12}
Methylene iodide	Reaction, no results.			
Tribromhydrin	29° 30′	43.87	38.00	76.18
α-Br-naphthalene	37° 30′	44.16	41.57	76.59
α-Cl-naphthalene	30° 00′	40.65	40.24	74.90
Iodobenzene	Reaction, no results.			
Bromoform	22° 15′		40.35	77.30

Average value of A_{13}, (all independent) = 76.16

TABLE VIII

Liquid-Air-Soda Lime Glass Contact Angles, θ_{12}
Adhesion tension values, liquid-soda lime glass, A_{12}

Organic liquid	θ_{12}	S_2	A_{12}
Acetylene tetrabromide	21° 15′	49.07	45.71
Tribromhydrin	17° 00′	44.76	40.68
α-Br-naphthalene	5° 00′	44.00	44.00
α-Cl-naphthalene	10° 15′	41.20	40.20
Iodobenzene	0°	39.10	> 39.10
Bromoform	16° 30′	40.93	39.24

By making use of the determined adhesion tension of water for silica and for lead glass, the adhesion tension of several other organic liquids for these solids were obtained and are given in Tables IX and X. The data of Table XI compares the values of the adhesion tension of several liquids as determined by this, the microscopic method, with those obtained by the Bartell-Osterhof displacement pressure (fine pore) method. It should be pointed out that the silica used in the latter method was specially treated tripoli or diatomaceous earth instead of transparent quartz. This would surely affect the results to a certain degree for the natures of the two surfaces would not be the same. A comparison should therefore be made on the basis of comparative values. For instance, the adhesion tension of water as determined by the two methods differs by nearly 7 dynes, a corresponding deviation holds also for the other liquid systems. Further evidence that the difference in values may be due to the different natures of the two forms of the silica is found in the work by Bartell and Miller[1]. With the displacement pressure method the adhesion tension of water for fine sand was found by them to be 74.10 dynes, a value even lower than that found by this method for fused quartz. With the above in mind, it is quite apparent that the values for the different liquids agree very well, which fact gives substantial evidence as to the soundness of both methods, their fundamental formulations, and

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[1] Bartell and Miller: unpublished.

developments, and at the same time indicates that the so-called adhesion tension of a liquid for a solid represents a specific and definite property of that system.

TABLE IX

Interfacial Contact Angles, Liquid-Water-Silica, θ_{23}
Adhesion tensions, organic liquid-silica, A_{12}

Liquid	A_{12}	θ_{23}	S_{23}	A_{12}
Water	75.92			
Amyl alcohol		55° 30'	4.96	73.13
Ethyl carbonate		55° 00'	12.65	68.74
Butyl acetate		45° 00'	13.17	66.60
Nitrobenzene		42° 30'	25.32	57.25
Toulene		35° 00'	35.86	46.54
Benzene		28° 40'	34.76	45.43
Carbon disulfide		42° 30'	48.10	40.46
Carbon tetrachloride		25° 15'	44.50	35.67
Hexane (synthetic)		25° 30'	51.00	29.90

TABLE X

Interfacial Contact Angles, Liquid-Liquid-Lead Glass
Adhesion tension, organic liquid-lead glass, A_{12}

Liquids	A_{13}	θ_{23}	S_{23}	A_{12}
Water	76.16			
Amyl alcohol		0°	4.96	<71.00
Ethyl carbonate		0°	12.67	<63.25
Butyl acetate		0°	13.17	<62.75
Nitrobenzene		27° 30'	25.32	53.50
Toluene		26° 30'	35.86	43.82
Benzene		0°	34.76	<41.66
Carbon disulfide		33° 40'	48.10	44.25
Hexane		36° 30'	51.00	34.92

TABLE XI

Comparison of Adhesion Tension Values; Fine Pore vs. Microscopic Methods

Liquids	A_{12} Fine pores	A_{12} Microscopic
Water	82.82	75.92
Butyl acetate	73.45	66.60
Carbon tetrachloride	40.69	35.67
Toluene	54.70	46.54
Benzene	52.43	45.43
Carbon disulfide	45.94	40.46

Conclusions

It is believed that this investigation has given the following rather conclusive evidences:—

1.—That equilibrium contact angles are formed when solid-liquid-air phases are in contact; likewise definite contact angles are formed between liquid-liquid-solid phases. These angles can be formed within capillary tubes; they are quite independent of the size of the tubes and can be measured fairly accurately.

2.—That the adhesion tension as measured is specific and definite for a given solid-liquid system.

3.—That the formulations used in the determination of adhesion tension were justified.

4.—That the data obtained by the microscopic method show good agreement with the results obtained by the Bartell-Osterhof pressure of displacement method and tends to substantiate the correctness of the assumptions made in connection with their work.

Department of Chemistry,
University of Michigan.

A STUDY OF THE ADSORPTION OF SUGARS AND
NITROGENOUS COMPOUNDS[1]

BY VASILY KNIASEFF

The purpose of the present work is to study the phenomena of adsorption of sugars and nitrogenous compounds and to obtain data particularly on the question of specificity of adsorption and the influence of certain factors which appear to be of practical importance.

We may divide our work into two parts. We shall first present material on the adsorption of different sugars on Norit and on fuller's earth. In the second part we shall give our results on the adsorption of nitrogenous compounds by fuller's earth only. In both studies we determined the effects of different factors on the phenomenon of adsorption, limiting our work practically to those factors which influence the liquid phase.

We chose, because of its convenience, to analyze by appropriate method the solutions before and after adsorption. In some cases volumetric and in other cases gravimetric methods were used. For analyzing sugar solutions titration with Fehling's solution according to the method outlined by Leach[2] was used. The solutions of nitrogenous compounds were analyzed by direct weighing or by titration.

Procedures used for determining Adsorption

Charcoal (Norit) and fuller's earth were used as adsorbents. Both adsorbents were used without thorough purification; fuller's earth was washed, however, several times with water, dried at 140° C, and passed through 200-mesh sieve. Therefore the adsorptions were of such kind as are used in commercial practice.

Fifty cc. of .029 molar solutions of sucrose, lactose, maltose, glucose, levulose, and galactose were placed with 1 gram of charcoal in Erlenmeyer flasks and shaken for a period of one-half hour; the same amount of solution was used for shaking with 1 gram of dried fuller's earth for one and one-half hours. Duplicate experiments in each case were run in parallel. The solutions after shaking were rapidly filtered through a Gooch crucible by suction. In order to obtain exact results, the following precautions were taken in filtration of solution: several cubic centimeters were passed through the filter paper and discarded; also the vacuum was kept as low as possible and constant. The filtrate was analyzed by titration against Fehling's solution.[3]

The amount of sugar adsorbed was calculated in the following way. The amount of sugar found by titration in a portion of the filtrate from adsorbent

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[2] Leach: "Food Analysis."

[3] Leach: "Food Analysis."

treated solution was subtracted from the amount of sugar present in an aliquot portion of original sugar solution. The Fehling's solution was standardized separately for each type of sugar solution. The duplicate titration agreed to within hundredths of cubic centimeter.

In carrying out the experiments on adsorption of nitrogenous compounds by fuller's earth, there were some variations in the procedure and analysis of the filtrate.

In the analysis of caffeine and urea a direct weighing method was used. Ten cubic centimeters of the filtrate were placed in a weighed crucible and evaporated to dryness in a drying oven and reweighed to constant weight. The crucibles were ignited and weighed again in order to determine if any amount of the adsorbent had passed through the filter. The difference between the second and the last weight was taken as the amount of the substance in 10 cc. of the solution. In order to verify the accuracy of the method, 10 cc. of the original standard solution were treated in the same way and very close checks were obtained. In the analysis of piperidine the titration method was used with methyl orange as indicator.

Rate of Adsorption

In making adsorption tests it is important to know the time required for equilibrium to be established between the amount of adsorbed solute on the adsorbent and the amount of solute in solution.

A series of solutions of the same concentration of lactose were shaken for different periods of time with 1 gr. of charcoal and with 1 gr. of fuller's earth. The results of the experiment are exhibited in Tables I and II.

From following tables it is easy to see that the amount of lactose adsorbed by charcoal is almost constant after fifteen minutes of shaking, while the adsorption by fuller's earth is not complete in an hour.

TABLE I

Rate of Adsorption of Lactose by Charcoal[1]

Time of shaking	¼ hour	½ hour	¾ hour	1½ hour
Amount of adsor. sugar in grs.	.0844	.0822	.0844	.0844
Concentration of solution at equilibrium in mmols.	27.5657	27.5710	27.5657	27.5657
Concentration of adsorbent at equilibrium in grs.	1	1	1	1

[1] 1 gr. of charcoal was shaken with 50 cc. of .029 mol. solution of lactose at natural pH.

TABLE II

Rate of Adsorption of Sugars by Fuller's Earth[1] (Lactose)

Time of shaking	¼ hour	½ hour	¾ hour	1½ hour
Amount of adsor. sugar in grs.	.0024	.004	.0152	.0167
Concentration of solution at equilibrium in mmols.	27.1933	27.7999	27.7578	27.7537
Concentration of adsorbent at equilibrium in grs.	1	1	1	1

Maltose

Time of shaking	½ hour	1½ hour
Amount of adsorbed sugar in grs.	.0144	.166
Concentration of solution at equilibrium in mmols.	27.7579	27.3389
Concentration of adsorbent at equilibrium in grs.	1	1

Relative Adsorption of Different Sugars by Charcoal and Fuller's Earth

The next step in our study was to determine the relative adsorption of different sugars by the two adsorbents studied. The results of experiments on different sugars are given in Tables III and IV.

TABLE III

Adsorption of Different Sugars by Charcoal[2]

Names of sugars:	Maltose	Lactose	Sucrose	Glucose	Galactose	Levulose
Mol. weights	360.25	360.25	342.18	198.4	180.13	180.13
Adsor. from .029 m. sol. grs.	.0844	.0825	.0816	.0375	.0375	.0366
mmols.	.2343	.2290	.2388	.1890	.2049	.2036
Concentration of solution at equilibrium in mmols.	28.7657	28.7710	28.7612	28.8110	28.7951	28.7964
Concen. of adsor. at equilibrium in grs.	1	1	1	1	1	1

[1] 1 gr. of fuller's earth was shaken with 50 cc. of .029 mol. solution of lactose and maltose at natural pH.

[2] ½ hour of shaking; 1 gr. of charcoal.

TABLE IV

Adsorption of Different Sugars by Fuller's Earth[1]

Names of sugars:	Maltose	Lactose	Sucrose	Glucose	Galactose	Levulose
Mol. weights	360.25	360.25	342.18	198.4	180.13	180.13
Adsor. from .029 M. sol.						
grs.	.01388	.01422	.0144	.01254	.00196	.00182
mmols.	.0385	.0395	.0421	.0632	.0109	.0101
Concentration of solution at equil. in mmols.	28.9615	28.9605	28.9579	28.9368	28.9891	28.9899
Concen. of adsor. in grs.	1	1	1	1	1	1

The results of these experiments show that charcoal adsorbs different sugars about equally but that fuller's earth adsorbs certain sugars much more readily than others.

Effect of pH on the Adsorption of Sugars by Charcoal and Fuller's Earth

A series of equivalent concentration of lactose and glucose solutions but with different adjusted pH values were prepared by the indicator method and a series of tests were made on each solution. Fifty cubic centimeters of the solution of .029 M. concentration were placed with 1 gr. of charcoal or fuller's earth in Erlenmeyer flasks and shaken for one half hour; the filtrates were analyzed as before. The results of these tests are given in Tables V-VIII.

TABLE V

The Effect of pH of Solution on the Adsorption of Lactose by Charcoal

pH of original solution	6.9	5.4	4.5	4.0
pH of filtrate	8.4	5.6	4.9	5.6
Amount of adsorbed sugar in:				
grs.	.1270	.1382	.1344	.14385
mmols.	.3525	.3836	.3731	.3993
Concentration of solution at equilibrium in mmols.	28.6475	28.6164	28.6269	28.6007
Concentration of adsorbent at equilibrium in gr.	1	1	1	1

The results of the experiments show that the adsorption of lactose by charcoal is not greatly affected by change of pH in the acid range with a tendency toward higher adsorption when the pH is lower.

Different results were obtained with fuller's earth as adsorbent, which can be seen from Table VI.

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[1] 1½ hours of shaking; 1 gr. of fuller's earth.

TABLE VI

The Effect of pH of Lactose Solution on Adsorption by Fuller's Earth and Change of pH of Solution

pH of original solution	4.1	5.5	7.4
pH of filtrate	5.6	5.6	7.1–7.0
Amount adsorbed in grs.	− .00027	− .00018	+ .00237
in mmols.	− .000007	− .0000053	+ .0000069

The data show that adsorption decreases with diminishing value of pH of solution; also negative adsorption was observed at pH 4.1 and 5.5.

TABLE VII

Adsorption of Glucose by Fuller's Earth at Different pH of Solution and Change of pH of Original Solution

pH of original solution:

4.0	4.3	5.5	6.4	6.75	7.4	8.4

pH of filtrate:

6.9	6.85	6.9	6.95	6.8	6.95	6.9

Adsorption in mgrs:

4.81	4.65	3.99	3.83	3.65	3.01	2.84

Adsorption in mmols:

.0247	.0234	.0201	.0193	.0184	.0152	.0143

Concentration of solution at equilibrium in mmols.

28.9753	28.9766	28.9799	28.9807	28.9816	28.9848	28.9857

Concentration of adsorbent at equilibrium in grs.

1	1	1	1	1	1	1

It can be seen from this table that a regular increase of adsorption with decrease of pH value of original solution took place, although this change is very negligible, almost zero.

Adsorption of Nitrogenous Compounds

Experiments were next conducted in order to study the adsorption of nitrogenous compounds by fuller's earth. For the present work sufficiently soluble nitrogenous compounds which were readily available were chosen. The largest number of experiments were done with caffeine, which possesses

amphoteric properties. $(K_a = >1 \times 10^{-14}; K_b = 4 \times 10^{-14})$. As it was observed by Grettie[1] that fuller's earth adsorbs only basic substances, therefore three other nitrogenous compounds which possess different basic properties from caffeine were used for comparative study. These substances were piperidine, which is strongly basic $(K_b = 1.2 \times 10^{-14})$, and urea $(K_b = 1.5 \times 10^{-14})$ which is slightly basic.

We followed almost the same scheme of work as that used in case of adsorption of sugars; the only difference being that we studied the influence of some other factors, which affect adsorption besides those which were mentioned in the case of adsorption of sugars.

Rate of Adsorption

In the study of the rate of adsorption of nitrogenous compounds the same general method was applied as in the case of sugars. Twenty-five cc. of .01 M caffeine solution were shaken with .1 gr. of fuller's earth for different periods of time, the results obtained are given in Table VIII.

<div align="center">TABLE VIII</div>

<div align="center">Rate of Adsorption of Caffeine by Fuller's Earth</div>

Time of shaking in minutes			
3	5	10	38
Amount of adsorption in grs.:			
.0049	.0053	.0054	.0056
Amount of adsorption in mmols.:			
.0232	.0251	.0255	.0260
Concentration of solution at equilibrium in mmols:			
9.9768	9.9749	9.9745	9.9740
Concentration of adsorbent at equilibrium in grs.			
.1	.1	.1	.1

The experiments demonstrate that the equilibrium is reached after a few minutes of shaking.

The Effect of pH of Solution on Adsorption of Caffeine by Fuller's Earth

A series of 25 c.c. of .01 M concentration of caffeine were shaken for five minutes with .1 gr. of fuller's earth. The results of these experiments are given in the Table IX.

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[1] J. Am. Chem. Soc., **50,** 668 (1928).

TABLE IX

Adsorption of Caffeine at Different pH of Solution

pH of original solution:

4	4.7	5.4	6.4	6.9	7.3	7.9	8.8	9.4

pH of filtrate:

7.9	7.1	7.2	7.4	7.2	7.2	7.2	7.5	9.0

Caffeine adsorbed in mgrs.:

5.43	5.58	5.33	5.48	5.33	5.33	5.33	5.38	4.88

Caffeine adsorbed in mmols.:

.0255	.0263	.0251	.0251	.0251	.0251	.0251	.0253	.0229

Concentration of solution at equilibrium in mmols.:

9.9745	9.9737	9.9749	9.9749	9.9749	9.9749	9.9749	9.9747	9.9771

Concentration of adsorbent at equilibrium in gr.

.1	.1	.1	.1	.1	.1	.1	.1	.1

These results show that practically no change of adsorption of caffeine with change of pH value could be observed.

Influence of Mass of Adsorbent on the pH of Solution

A series of 25 c.c. of .01 M solution of pure caffeine were shaken with the following quantities of fuller's earth: .5 g., .1 g., .05 g., and .01 g.

The results of experiment are given in Table X.

TABLE X

Amount of fuller's earth used in grs.:

.5	.25	.1	.05	.01

Caffeine adsorbed in mgrs.:

19.1	9.45	7.48	3.6	.48

Caffeine adsorbed in mmols.:

.090	.0555	.0352	.0168	.0022

Concentration of solution at equilibrium in mmols.:

9.9100	9.9445	9.9648	9.9832	9.9978

Initial pH of solution:

6.8	6.8	6.8	6.8	6.8

pH of filtrate:

8.4	7.6	7.4	7.0	6.8

This table shows that the change of pH of solution (Increase) is proportional to the amount of earth added.

The Effect of the Nature of the Solvent

It was observed that the nature of solvent has a great effect on adsorption of solute. This may be seen clearly if we compare the results reported here on adsorption of nitrogenous compounds in alcohol solution with those obtained by Grettie,[1] who performed experiments on the adsorption of the same compounds only from water solution. In both cases the conditions of experiment were identical, namely 25 c.c. of .01 M solution were shaken for five minutes with .5 gr. of fuller's earth. The results are shown in Table XI.

TABLE XI

The Effect of the Nature of the Solvent on the Adsorption of Caffeine, Piperidine, and Urea

Names of compounds:	Piperidine	Caffeine	Urea
Amount adsorbed from water solution in %:	73.8	92.3	5
Amount adsorbed from water solution in mmols.:	.1840	.0923	.0125
Concentration of solution at equilibrium in mmols.:	9.8160	9.9077	9.9875
Amount adsorbed from alcohol solution in %:	33.6	73.5	.95
Amount adsorbed from alcohol solution in mmols.:	.0347	.0735	.0024
Concentration of solution at equilibrium in mmols.:	9.9653	9.9265	9.9976
Concentration of adsorbent at equilibrium in grs.:	.5	.5	.5

The experimental data shows that the adsorption of nitrogenous compounds is less in alcohol solution than in water solution.

Displacement Type of Adsorption

We thought when caffeine is shaken with fuller's earth the caffeine unites with the earth and calcium is liberated.

In order to test out is our idea true we carried out several experiments on adsorption of caffeine by fuller's earth and analyzed the filtrate for both caffeine and calcium. These experiments were performed with both washed and unwashed fuller's earth with solutions of different concentration and with solutions of different pH values. The results obtained are indicated in Tables XII-XIV.

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[1] J. Am. Chem. Soc., 50, 668 (1928).

TABLE XII

The Displacement of Calcium by Caffeine from Fuller's Earth

Washed fuller's earth	Unwashed fuller's earth

Caffeine adsorbed in grs.:

.1188	.1225

Caffeine adsorbed in mmols.:

.56	.58

Calcium found in filtrate in gr.:

.000278	.000991

Calcium found in filtrate in mmols.:

.00695	.0247

The results indicate some displacement of calcium from fuller's earth but the quantity is negligible and not directly proportional to the amount of caffeine adsorbed.

The experiment on displacement was repeated with small variation, namely different concentrations of caffeine solutions were used. The results are given in Table XIII.

TABLE XIII

Displacement of Calcium in Adsorption of Caffeine at Different Concentration of Solution

(1 gr. of fuller's earth used)

Concentration of solution in mols.:

.1	.05	.01

Caffeine adsorbed in grs.:

.0696	.0592	.02008

Caffeine adsorbed in mmols.:

.327	.278	.093

Calcium found in filtrate in mmols.:

0	.0033	.0155

Also experiments on the displacement of calcium by caffeine at the different pH of solution were carried out and the following results were obtained which are given in Table XIV.

TABLE XIV

Displacement of Calcium in Adsorption of Caffeine at the Different
pH of Solution[1]

pH of Initial Solution:

4.0	7.1	7.9

Caffeine adsorbed in grs.:

.0727	.094	.096

Caffeine adsorbed in mmols.:

.343	.442	.451

Calcium found in filtrate in mgrs.:

.71	.74	.53

Calcium found in filtrate in mmols.:

.017	.018	.013

The amount of calcium present in the filtrate was irregular and seems to have nothing to do with the pH of solution; the displacement of calcium does not conform to the law of multiple proportion.

Summary

1). In the adsorption of sugars by charcoal (Norit) equilibrium is reached in a few minutes. Adsorption of sugars by fuller's earth does not reach equilibrium in less than an hour.

2). The various sugars tested were adsorbed about equally by charcoal but fuller's earth adsorbed certain sugars much more readily than others.

3). The adsorption of lactose by charcoal is not greatly affected by change of pH in the acid range, but there is a tendency toward higher adsorption when the pH is lower. The adsorption of lactose by fuller's earth decreases with diminishing values of pH. Negative adsorption of this sugar was observed at pH 4.1 and pH 5.5. In case of the adsorption of glucose by fuller's earth a regular but very small increase of adsorption with decrease of the pH value of original solution was noted.

4). In the adsorption of caffeine by fuller's earth the equilibrium is reached in a few minutes of shaking.

5). Adsorption was practically unaffected by pH of original solution, when 25 c.c. of .01 mol. solution of caffeine were shaken with .1 gr. of fuller's earth.

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[1] 1 gr. fuller's earth shaken with 25 cc. of .05 M. sol. caffeine.

6) There is a shift of pH of original solution of caffeine after shaking with fuller's earth; this shift is also proportional to the amount of fuller's earth used.

7). The adsorption of three typical nitrogenous compounds by fuller's earth is less from alcoholic solution than from water solution.

8). Calcium was found in the filtrate of caffeine solution shaken with fuller's earth; the amount of calcium was practically negligible and not directly proportional to the amount of caffeine adsorbed; the amount of calcium present in the filtrate was irregular at the different pH values of the caffeine solution.

This work was done under the direction of Dr. R. J. Williams, to whom I wish to express my sincere thanks for his able guidance and helpful suggestions.

Department of Chemistry,
University of Oregon,
Eugene, Oregon.

CHEMICAL ACTIVITY AND PARTICLE SIZE

II. The Rate of Solution at Slow Stirring of Anhydrite and Gypsum*

PAUL S. ROLLER**

Natural anhydrite is an unstable phase[1] of calcium sulphate at 20°C. and is about $1\frac{1}{2}$ times as soluble as gypsum,[2] yet its rate of solution is much less than that of the dihydrate.[3,4] It seemed possible that the dissolution of the anhydrite might be activated by a reduction in the particle size, entirely apart from the ordinary effect resulting from an increase in specific surface.

Three reasons appeared to lead to this conclusion, as follows:

1. The Nernst-Brunner[5,6] theory postulates that the rate of solution of a solid in a liquid is governed by the rate of diffusion from a saturated layer adjacent to the surface through an adhering film. By calculation the thickness of this film at ordinary stirring speeds (100 to 500 r.p.m.) is 20 to 50 microns.[6,7] It seemed altogether reasonable to suppose that, other conditions remaining the same, the thickness of this film in contact with particles of the order of 1 to 50 microns in size would be modified from its value at a plane surface. Hence, since the specific rate of solution according to the Nernst theory varies inversely as the film thickness, a specific effect should be observed for such particles beyond the effect due to changes in the surface exposed.

2. Probably the strongest support of the Nernst diffusion theory of heterogeneous reaction has been in the results of Van Name and his co-workers[8] which showed that the relative rate of oxidation of a number of metals in KI_3 solution was independent of the nature of the metal; on the other hand it must be remembered that the same authors[9] have found that the rate of oxidation by ferric sulphate and chromic acid in H_2SO_4 and ferric chloride in HCl solution was in the same order as the e.m.f. series of the metals. This result is contrary to the assumption of the Nernst theory that reaction at the solid-liquid interface is instantaneous.

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[1] van't Hoff: Z. physik. Chem., 45, 257 (1905).

[2] Roller: J. Phys. Chem., 35, 1133 (1931).

[3] McCaleb: Am. Chem. J., 11, 31 (1889).

[4] Wildermann: Z. physik. Chem., 66, 445 (1909).

[5] Nernst: Z. physik. Chem., 47, 52 (1904).

[6] Brunner: Z. physik. Chem., 47, 56 (1904).

[7] Wagner: Z. physik. Chem., 71, 401 (1910).

[8] Van Name and Edgar: Am. J. Sci. (4) 29, 237 (1910); Van Name and Bosworth: 32, 207 (1911); Van Name and Hill: 36, 543 (1913); Van Name: 43, 449 (1917).

[9] Van Name and Hill: Am. J. Sci. (4), 42, 301 (1916).

Similarly, the rate of solution of anhydrite in water may be governed not by diffusion but by the rate of reaction at the surface. That this is the situation for the solution of metals in acids is indicated by the fact that the rate of solution is independent of the rate of stirring when the latter is sufficiently high;[10] this has also been observed for benzoic acid in water at a stirring speed above 400 r.p.m.[4] The fundamental importance of the rate of reaction at the surface is also indicated by the fact that different crystal faces of the same substance have different rates of solution,[7,11] although in contrast to the early considerations of Curie and Wulff the saturation solubility for each of these faces is the same or imperceptibly different.[12,18,35]

As regards the interaction at the surface, recent evidence indicates that such interaction between a solid and a fluid takes place not uniformly over the surface of the solid but at "active spots" as first propounded by Taylor.[13] These active spots may correspond to the "crystal defects" observed by Smekal,[14] and also to the edges and corners as observed by Volmer[15] and theoretically considered by Stranski,[16] Kossel,[17] and Brandes.[18] Assuming that the surface activity is nil, then, if the rate of solution were governed solely by reaction at the edges, it should increase with the inverse square of the particle size, and if governed by the corners, with the inverse cube of the particle size.[19] If as seems probable for the solution process, the surface activity plays a part, then, assuming the latter to be constant for different sizes of particles, the rate should increase inversely with a power of the particle size lying between 1 and 3.

3. Since many individual microscopic particles constitute a given weight of solute, the physical interaction of these particles, differing in general with particle size, will have an effect on the rate of solution. In this work the microscopic crystals were in most cases contiguous to one another. Consequently, neighboring particles will affect the availability of the solvent to an individual particle under consideration. The degree of the interference will depend on the particle size (less than a given value) and on conditions of the experiment.

Results of this present work show, as previously found at a stirring speed of 470 r.p.m.,[2] that there is an enhanced or activated rate of solution for both anhydrite and gypsum with decrease in particle size below 50 microns.

[10] Centnerszwer and Zablocki: Z. physik. Chem., **122**, 455 (1926); Centnerszwer and Straumanis: **128**, 369 (1927); Centnerszwer: **137**, 352 (1928); **141A**, 297 (1929).

[11] Becke: Tschermak Min. and Pet. Mitt., **11**, 349 (1890); Schenk: Z. Min. **1900**, 313; Rinne: Cent. Min., **1904**, 116; Korbs: Z. Krist., **43**, 434 (1907); Gross: **57**, 145 (1922); Glauner: Z. physik. Chem., **142**, 67 (1929); Tammann and Sartorius: Z. anorg. Chem., **175**, 197 (1929).

[12] Valeton: Ber. math. physik. sächs Ges. Leipzig, **67**, 1915; Physik. Z., **21**, 606 (1920).

[13] Taylor: Proc. Roy. Soc., **108A**, 105 (1925); J. Phys. Chem., **30**, 145 (1926).

[14] Smekal: Physik. Z., **26**, 707 (1925); Z. angew. Chem., **42**, 489 (1929; Z. Elektrochemie, **35**, 567 (1929).

[15] Volmer: Z. physik. Chem., **102**, 270 (1923).

[16] Stranski: Z. physik. Chem., **135**, 259 (1928); **11B**, 342 (1930).

[17] Kossel: Nachr. Ges. Wiss. Göttingen math. physik. Kl., **1927**, 135.

[18] Brandes: Z. physik. Chem., **126**, 198 (1927).

[19] Schwab and Pietsch: Z. Elektrochemie, **35**, 573 (1929).

Briefly, as regards the above theories, it is demonstrated that the Nernst film, if it exists, is considerably smaller than the expected 20 to 50 microns in thickness. In fact, it is less than 0.2 of a micron—i.e., less than one-hundredth of the theoretically accepted value. Evidence is presented from the recent literature which substantiates this conclusion and, still further, indicates that any film at the surface must be indefinitely thin, of the order of a monomolecular adsorption layer. Consequently in heterogeneous reaction the supposition of diffusion through an adhering Nernst film as the fundamental *modus operandi* is untenable, and can not be used to explain the results of this work.

With the solute added dry to the solvent, the enhanced effects appear to be intimately associated with the structure of the dissolving sediment. When the solute (anhydrite) is initially dispersed in a small amount of water, this situation also obtains for particles between 8 and 50 microns in size. However, for particles below 8 microns, the enhanced rate of solution is apparently due to the effect of edges and corners superimposed upon solution directly from the surface, apparently by way of active centers of the latter.

Apparatus

The apparatus, which is the same as that previously used,[2] is shown in Fig. 1. The slightly tapered cylindrical Kavalier glass beaker was 4.9 cm. in diameter, at the lower end, and 13 cm. deep, the water reaching to a height of 5.5 cm. above the bottom. The stirrer that passed through a split ebonite cover consisted of a 5.5-mm. solid glass rod, to the bottom of which was fused a hollow glass inverted "T," the arms
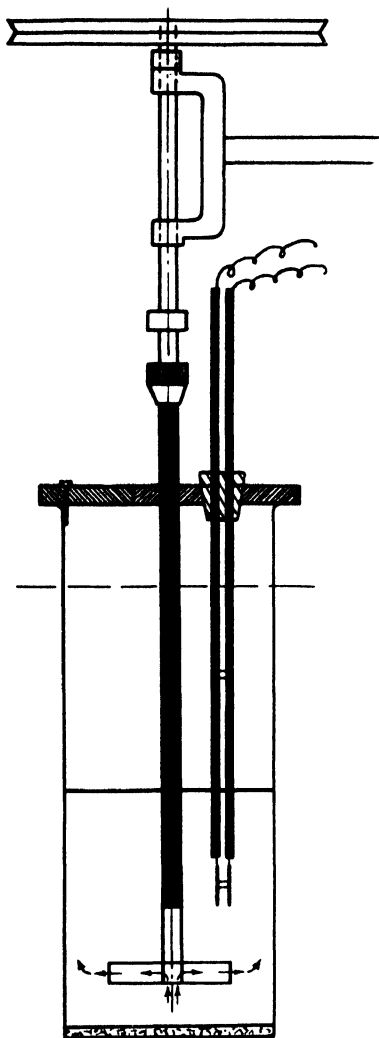
FIG. 1

of which were 3 cm. across. With rotation of the stirrer, a circulation of the water was set up in the hollow T as shown by the arrows. The end of the T was in all cases 12 mm. above the bottom of the beaker. The thickness of the dissolving sediment, 0.4 to 1.5 mm., was negligible in comparison to this distance.

The conductivity of the solution was measured by unprotected platinized platinum electrodes that were frequently checked. The electrodes were

15 mm. long by 9 mm. across, the upper edge being 5 mm. below the surface of the water.

In some auxiliary experiments a cylindrical Pyrex beaker 5.3 cm. wide at the bottom and 10 cm. deep was used.

Materials

The distilled water had a conductivity that was checked before each experiment of 2-3 $\times$ 10^{-6} r.o.

The anhydrite was the same pure crystalline product as was used before.[2]* The gypsum was Baker's c.p. grade. Both materials were finely ground and then air-separated to secure the desired particle-size fractions. The gypsum

TABLE I

Microscopic Analysis of Particle Size Fractions of Anhydrite

Fraction

I	0–1	1–2	2–3	3–4			Microns
	56.2	11.9	12.3	19.6			Weight per cent
	96.2	2.5	0.8	0.5			Number per cent
II	0–1	1–2	2–3	3–4	4–5	5–6	Microns
	24.8	5.0	3.0	38.6	15.9	12.7	Weight per cent
	95.2	2.2	0.4	1.8	0.3	0.1	Number per cent
III	2–3	3–5	5–7	7–9			Microns
	2.6	22.2	24.3	50.9			Weight per cent
	25.2	50.5	13.4	10.9			Number per cent
IV	7–10	10–15	15–20				Microns
	3.4	40.3	56.3				Weight per cent
	16.4	55.2	28.4				Number per cent
V	15–20	20–25	25–30	30–40			Microns
	9.0	28.7	33.0	29.3			Weight per cent
	23.0	26.0	14.5	36.5			Number per cent
VI	26–35	35–55	55–80				Microns
	1.7	40.2	58.1				Weight per cent
	7.3	60.7	32.0				Number per cent
VII	85–100	100–150	150–200	200–250			Microns
	3.5	41.0	40.5	15.0			Weight per cent
	12.7	65.5	17.3	4.5			Number per cent
VIII	125–150	150–200	250–275				Microns
	2.8	53.1	44.1				Weight per cent
	11.4	67.2	21.4				Number per cent

* Courtesy of the U. S. Gypsum Co.

TABLE II

Microscopic Analysis of Particle Size Fractions of Gypsum

Fraction

I	0–1	1–2	2–3	3–4				Microns
	50.7	28.2	17.0	4.1				Weight per cent
	92.8	6.5	0.7	0.1				Number per cent

II	0–1	1–2	2–3	3–4	4–5	5–7	7–9	Microns
	6.5	4.2	10.1	20.6	29.7	14.3	14.6	Weight per cent
	84.6	6.7	3.8	2.8	1.6	0.3	0.2	Number per cent

III	3–6	6–8	8–10	10–12	12–15			Microns
	3.8	18.1	23.5	27.4	27.2			Weight per cent
	33.4	29.5	19.2	11.5	6.4			Number per cent

IV	5–10	10–13	13–16	16–19	19–22	22–25		Microns
	3.5	8.2	22.3	21.2	22.3	22.5		Weight per cent
	28.4	19.4	25.4	11.9	9.0	5.9		Number per cent

V	12–18	18–24	24–30	30–36	36–42	42–50	50–60	Microns
	2.0	3.3	23.5	34.0	11.0	14.5	11.7	Weight per cent
	18.4	10.2	33.7	26.5	5.1	4.1	2.0	Number per cent

VI	26–35	35–55	55–80					Microns
	2.3	55.4	42.3					Weight per cent
	10.0	71.6	18.4					Number per cent

VII	100–150	150–200	200–250					Microns
	19.6	75.1	5.3					Weight per cent
	33.3	65.0	1.7					Number per cent

VIII	150–250	250–400						Microns
	30.5	69.5						Weight per cent
	50.8	48.2						Number per cent

was separated in an air analyzer;[20] later an enlargement of this apparatus was constructed[21] that permitted the securing of considerable quantities of the fractions in a much shorter time; this apparatus was used for the anhydrite separations. The two coarsest fractions between 150 and 250 microns were obtained by sieving between the 50 and 200 mesh sieve. These fractions in spite of prolonged sieving still retained appreciable quantities of adhering "fines" that showed up in preliminary rate of solution measurements; the sieved fractions were therefore treated in the air analyzer, the fines being thus effectively removed.

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[20] Roller: U. S. Bureau Mines Tech. Paper, No. 490 (1931).
[21] Roller: Ind. Eng. Chem. Anal. Ed., 3, 212 (1931).
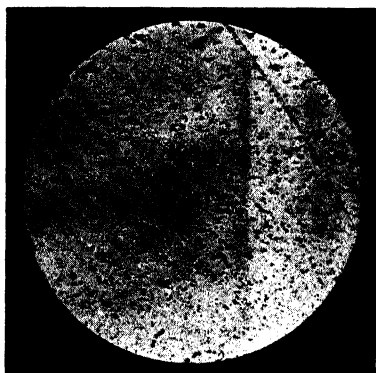
FIG. 2
335 ×
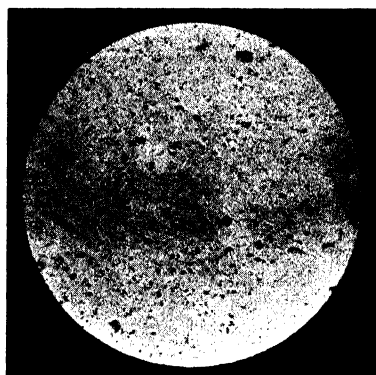
FIG. 3
335 ×
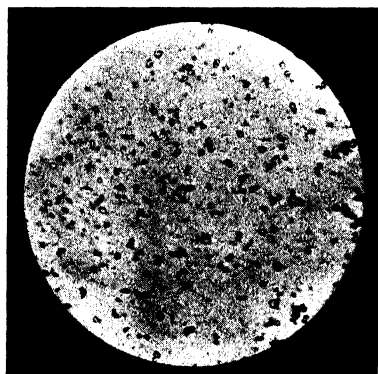
FIG. 4
335 ×
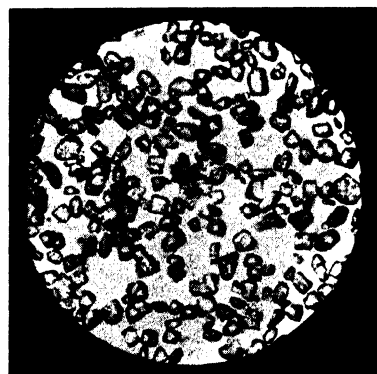
FIG. 5
335 ×
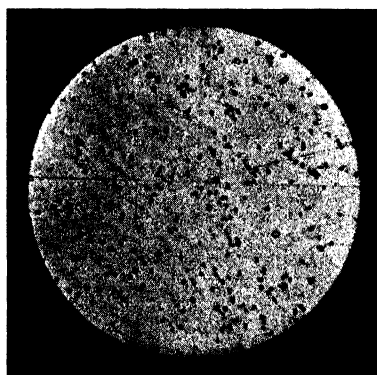
FIG. 6
45 ×
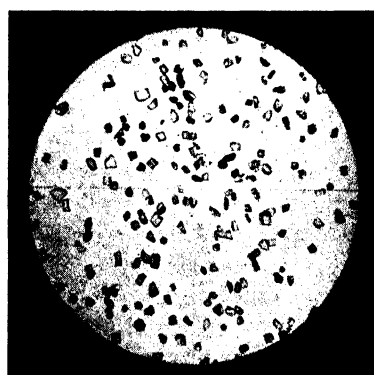
FIG. 7
45 ×
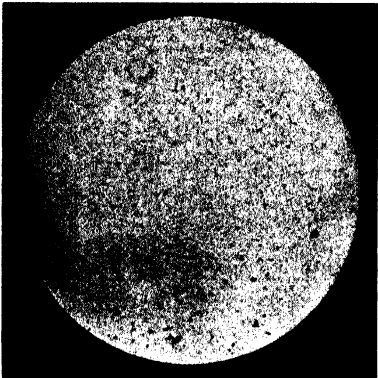
FIG. 8
335 ×
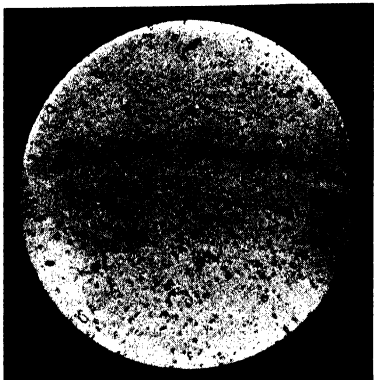
FIG. 9
335 ×
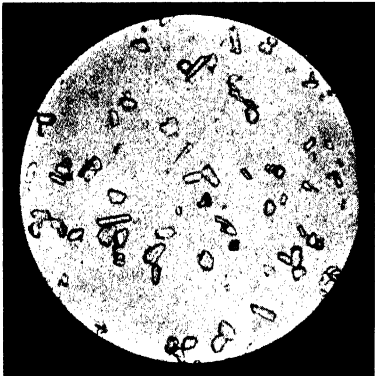
FIG. 10
335 ×
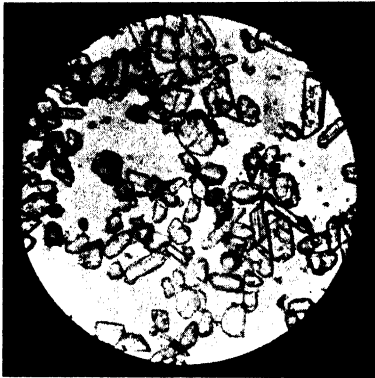
FIG. 11
335 ×
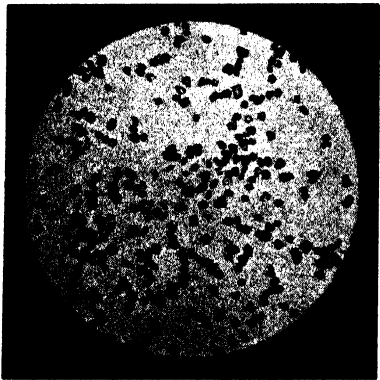
FIG. 12
70 ×
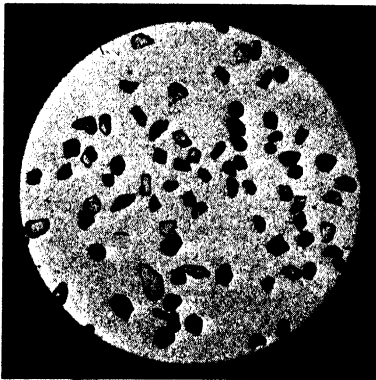
FIG. 13
70 ×

To counteract the dehydrating effect of the grinding and air separation, the gypsum fractions previous to microscopic measurement were superficially rehydrated by stirring with water at room temperature for 1 or 2 hours, filtered, washed with 50% alcohol, 95% alcohol, and ether, and dried at 70°C. The fractions then showed a specific conductivity of 1.965×10^{-3} r.o. at 20°C., the value found by Böttger[22] being 1.970×10^{-3} r.o. at 19.94.°

Figs. 2 to 7 are photomicrographs of the air-separated anhydrite fractions I to VI respectively, and Figs. 8 to 13 are of the same gypsum fractions. In Tables I and II are given summarized microscopic counts of the particles contained in the anhydrite and gypsum fractions, respectively. It should be noted that fraction II in each case overlaps fraction I due to "attrition" of the soft powder by the air current at this particle size separation.

The surface mean diameter, d_s, of each of these fractions, as previously,[2] is defined by equation (1) in which d is the arithmetic mean of the length and width of a particle and the summation is taken over all the measured particle sizes.

$$(1) \quad d_s = \Sigma d^3 / \Sigma d^2$$

The calculated values of d_s are shown in Table III.

TABLE III

Surface Mean Diameter of Anhydrite and Gypsum Fractions

Fraction	Anhydrite	Gypsum
I	1.10	1.10
II	1.89	3.22
III	5.9	9.8
IV	14.7	17.3
V	26.5	35.3
VI	53.8	53.1
VII	157	177
VIII	250	286

Method

The procedure in measuring the dissolution was the same as formerly[2] except that 100 c.c. of water instead of 135 c.c. was used and 0.8 gram was taken as a standard weight in place of 0.7 gram. Also, the stirring speed was now 130 r.p.m. instead of 470 r.p.m.

In these experiments the solute was added to the water in two different ways. After the solvent and powder had come to temperature in a water bath maintained at $20.0 \pm .03$°C. the solute was spread out in the weighing tube and was added to the water during stirring of the latter. In the second method of addition of the solute, the powder was first dispersed, generally with 2 c.c. of water, and the suspension added to the water in the beaker. For all fractions of the powder added dry, settling took place within a period of 5 seconds, the rotating stirrer helping to spread the powder over the bottom of the beaker.

[22] Böttger: Z. physik. Chem., **46**, 602 (1902).

Conductivity readings were converted into concentrations by means of Hulett's formula as before, but for concentrations below 0.1 gr./100 c.c. the somewhat more accurate data of Kohlrausch and Grüneisen[23] were used. All runs were made at least twice and the results averaged. The error of the average for the powder added dry was ± 4%; with fractions III and IV, between 5 and 15 microns, the results were somewhat erratic, due apparently, at the low rate of stirring, to the powder occasionally falling off in a lump to one side of the beaker or clinging at the surface. The discordantly low values thus obtained were neglected in obtaining the average. This "lumping" tendency of fractions III and IV which seemed to be influenced by the humidity was largely overcome by shaking and spreading the powder out in a large weighing tube and then uniformly adding it to the solution. Due to fluctuations the accuracy for these fractions was ± 8%.

With the powder dispersed in water the results for all the fractions were quite reproducible, the accuracy being ± 1%.

The average error in d_s was ± 8%; for fractions I and II the error was smaller than ± 4%.

Results for Anhydrite and Gypsum added dry

The time-concentration values for anhydrite and gypsum added dry are shown in Tables IV and V and are plotted in Figs. 14 and 15. It is seen that the rate of solution is initially high but falls off rapidly in the first two or

TABLE IV

Dissolution of 0.8 Gram of Anhydrite added dry to 100 c.cm. of Water at a Stirring Speed of 130 r.p.m.

	I	II	III	IV	V	VI	VII	VIII	Fraction
			Surface Mean Diameter						
	1.10	1.89	5.9	14.7	26.5	53.8	157	250	Microns
Min.			Grams CaSO₄ × 10²/100 c.c.						
0.1	.37	.59	.59	.45	.43	.30	.10	.07	
0.25	1.32	1.75	1.51	1.30	.97	.59	.16	.11	
0.50	1.77	2.33	3.02	2.22	1.38	.65	.21	.16	
1.0	2.33	2.85	5.17	3.28	1.75	.75	.28	.23	
1.5	2.70	3.33	6.42	3.92	1.95	.82	.34	.28	
2.0	2.98	3.60	7.25	4.35	2.08	.88	.39	.33	
3.0	3.42	4.02	8.25	5.03	2.17	.95	.48	.42	
4.0	3.75	4.30	9.06	5.52	2.38	1.01	.56	.51	
5.0	3.98	4.50	9.52	5.80	2.47	1.08	.65	.59	
6.0	4.22	4.70	9.83	6.00	2.58	1.14	.72	.66	
7.0	4.38	4.92	10.16	6.20	2.66	1.20	.81	.75	
8.0	4.60	5.15	10.45	6.42	2.76	1.26	.89	.83	
9.0	4.83	5.38	10.73	6.62	2.84	1.33	.98	.91	
10.0	5.02	5.58	11.08	6.81	2.92	1.40	1.06	.99	

[23] Kohlrausch and Grüneisen: Landolt-Börnstein Tab., 2, 1081 (1923).

Figure 14
Dissolution of Anhydrite Added Dry
0.8 gr. per 100 cc. at 130 r.p.m.
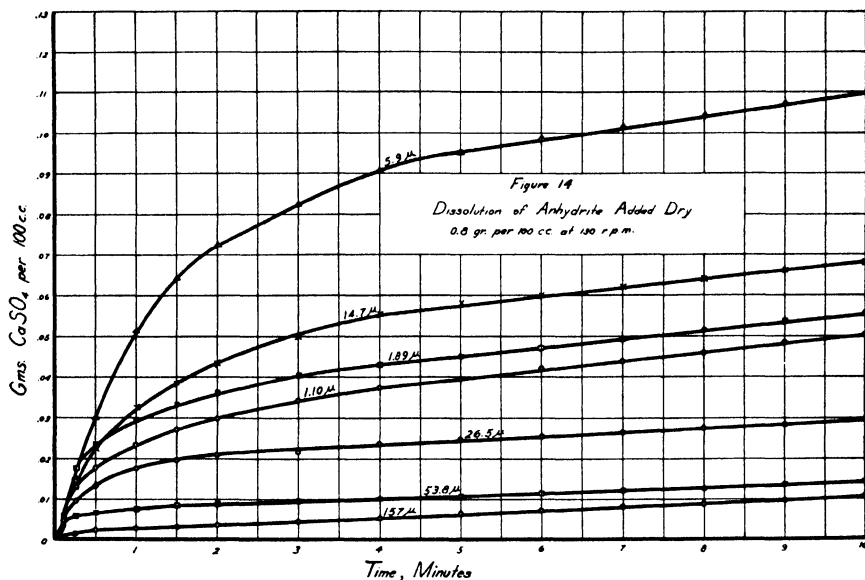
three minutes; thereafter the rate of increase in concentration is relatively slight and is about the same for the different fractions. During the settling period of less than 5 seconds the amount dissolved of the solute added dry is small; indeed, for the finer fractions I to IV, that is, below about 17 microns, there is an induction period of 4 or 5 seconds in which the amount dissolved is virtually nil.

The unexpected low rate of solution of the fine fractions I and II, i.e. below about 3 microns, should be noted. These fractions dissolve more

Figure 15
Dissolution of Gypsum Added Dry
0.8 gr. per 100 cc. at 130 r.p.m.
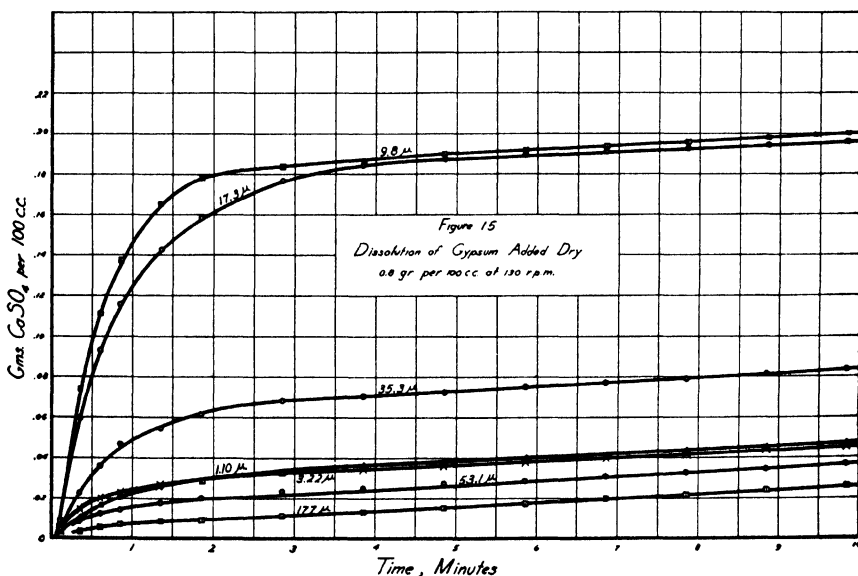
TABLE V

Dissolution of 0.8 gram of Gypsum added dry to 100 c.cm. of Water at 130 r.p.m.

	I	II	III	IV	V	VI	VII	VIII	Fraction
			Surface Mean Diameter						
Time	1.10	3.22	9.8	17.3	35.3	53.1	177	286	Microns
Min.	Grams CaSO$_4$ × 10^2/100 c.c.								
0.10	0.27	0.37	0.94	0.90	0.45	.41	.21	.09	
0.35	1.05	1.51	7.40	6.00	2.29	.91	.35	.20	
0.60	1.69	2.02	11.10	9.36	3.57	1.26	.61	.30	
0.85	2.08	2.26	13.76	11.64	4.67	1.47	.71	.38	
1.35	2.62	2.67	16.50	14.37	5.53	1.81	.85	.53	
1.85	2.95	2.91	17.91	15.91	6.20	2.02	.96	.68	
2.85	3.35	3.26	18.37	17.72	6.88	2.35	1.16	.95	
3.85	3.66	3.51	18.72	18.53	7.06	2.58	1.35	1.19	
4.85	3.96	3.74	18.97	18.75	7.26	2.75	1.55	1.41	
5.85	4.12	3.96	19.08	18.97	7.50	2.92	1.76	1.66	
6.85	4.31	4.17	19.35	19.07	7.73	3.12	1.98	1.90	
7.85	4.50	4.38	19.62	19.25	7.94	3.30	2.19	2.20	
8.85	4.68	4.58	19.84	19.41	8.08	3.45	2.39	2.48	
9.85	4.86	4.79	20.23	19.60	8.38	3.63	2.60	2.75	

slowly than the 14.7 micron fraction in the instance of anhydrite and more slowly than the 35.3 micron fraction in the instance of gypsum. The inertness of these fractions at slow stirring is therefore more pronounced for gypsum than for anhydrite. This fact is further evidenced by the closeness of the rate of solution of fractions III and IV of gypsum in contrast to the distinct difference for the similar fractions of anhydrite.

The above results for fractions I and II added dry can be understood if it is considered that solution takes place by penetration of the solvent into the sediment formed by the finely divided crystal grains. Owing to their mutual attraction, the particles constituting the dry fractions below about 3 microns tend to cluster together into ball-like aggregates;[20] on the other hand, this tendency rapidly diminishes with increase in size of particle so that it has largely disappeared in fraction III. As a result of this highly aggregated state of fractions I and II it is difficult for the solvent to penetrate the sediment (which will have formed rapidly by settling due to the same aggregation of the particles and in spite of their individual fineness), so that the rate of solution is extremely small.

Gypsum being softer than anhydrite, it may be expected that the stray fields of force at the surface are greater and consequently also the mutual attraction of the fine particles. This will explain the fact that fractions I and II of the dihydrate added dry to the solvent are relatively more inert than the corresponding fractions of anhydrite. In fact, in contrast to the other fractions, the rate of solution of fractions I and II under the slow stirring conditions is actually greater for anhydrite than for gypsum.

Conversely to the results at 130 r.p.m., the two finest fractions of anhydrite I and II (1.96 and 3.17 microns) added dry at the higher stirring speed of 470 r.p.m., showed a much greater rate of solution[2] than fraction III (7.56 microns). This difference is due to the fact that the penetration by the solvent of the sediment grains is relatively more effective with increase in the speed of stirring for the finer clustered grains than for the coarser. In the same way preliminary experiments showed that the rate of solution of fractions I and II of the gypsum added dry at the higher stirring speed was, in contrast to the result at slow stirring, considerably greater than that of the corresponding fractions of anhydrite. Thus it is seen that increase in the speed of stirring selectively increases the solution rate of the finest particles below about 5 microns when added dry to the solvent to a value approaching normal.

It seemed possible that the observed low rate of solution at slow stirring for fractions I and II of anhydrite and gypsum might be due to a tenaciously adsorbed air film. For example, Ehrenberg and Schultze[24] found that the displacement by water of the air film surrounding a finely divided soil and lampblack was a slow process. To test out this hypothesis the rate of solution of anhydrite fraction II (1.89 μ mean diameter) was measured in a heavy walled Pyrex beaker described above. After three-quarters of a minute, stirring was interrupted and the beaker evacuated at 30 mm. of mercury. Release of small air bubbles took place and terminated in the course of several minutes. Stirring was then continued and conductivity readings taken as before. For comparison the rate of solution was also measured by first dispersing the powder in 2 c.c. of water.

From the results which are shown in Table VI, it is seen that with removal of the air that doubtless adhered to the surface of the powder in the form of minute bubbles, the rate of solution increased, but the effect is quite small compared with that obtained by first dispersing the grains.

TABLE VI

Comparison of Dissolution of 0.8 Gram of Fraction II of Anhydrite
(1.89 microns) with and without Evacuation at 30 mm. Hg.

Grams $CaSO_4 \times 10^2/100$ c.c. after 6 min.

Added dry	4.41
Added dry with evacuation	6.05
Initially dispersed	16.97

In another type of experiment evacuation was carried out in a small thin bulb, the powder wetted in vacuo, and the contents added to the solvent by shattering the bulb. Here again the effect of a possible adhering air film was found to be negligible.

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[24] Ehrenberg and Schultze: Kolloid-Z., **15**, 183 (1914).

It may be noted at this point that just as for the anhydrite, a great increase in the rate of solution of fraction I of gypsum was obtained by first dispersing in 2 c.c. of water. With 0.8 of a gram thus taken for solution saturation was reached in slightly less than 1 minute.

Rate of Solution versus Particle Size for Anhydrite and Gypsum added dry

In determining the relative rate of solution of the different particle sizes, a definite method of comparison must be fixed upon. It was found that the initial rates of the different fractions could not be directly compared, first, because of the very rapid way in which they changed, and second, because of the presence of initial disturbances caused by the varying sedimentation and the presence in some cases of a slight induction period. Comparison of the times required to reach a definite concentration or to span a definite

TABLE VII

Comparison of Concentration Ordinates for Anhydrite added dry
at 130 r.p.m.

Fraction	Surface Mean Diameter microns	Grams taken for Solution	Concentration at 6 min. Gr. $CaSO_4 \times 10^2/100$ c.c.
I	1.10	0.8	4.22
		1.6	6.35
II	1.89	0.8	4.68
		1.6	6.75
		2.4	8.62
III	5.9	0.8	9.83
IV	14.7	0.8	6.00
		1.6	7.12
		2.4	8.55
V	26.5	0.8	2.58
		1.6	3.52
		3.2	5.32
VI	53.8	0.8	1.14
		1.6	1.65
		2.4	2.29
VII	157	0.8	.72
		1.6	.90
		2.4	1.08
VIII	250	0.8	0.67
		1.6	0.81

concentration interval was also ruled out because of the existence practically of two stages in the solution process, namely, an initially fast stage covering the first 2 or 3 minutes, and then a uniformly slow stage. It was in most cases impossible to confine the time comparisons for any two fractions to the same stage. Consequently, the method was pursued that was previously employed,[2] of comparing after a given time the concentration ordinates of multiple weights of a given fraction with the concentration of a standard weight of the next adjacent finer fraction. The assumption involved is that for a given fraction the rate of solution as measured by the concentration is proportional to the surface exposed. This appears to be borne out by the fact that for all the fractions, under the same set of conditions, equal increments in weight of solute resulted in equal increases in concentration in the range covered.

As larger quantities of the fractions were now available than heretofore, an ascending scale of multiple weights of 0.8, 1.6, 2.4, etc., grams was uniformly employed. A small correction to the surface of the solute for the amount dissolved was made as before.

TABLE VIII

Comparison of Concentration Ordinates for Gypsum added dry at 130 r.p.m.

Fraction	Surface Mean Diameter	Grams taken for Solution	Concentration Gr. $CaSO_4 \times 10^2/100$ c.c.	
			2.85	6.85 min.
I	1.10	0.8		4.31
II	3.22	0.8	3.22	4.17
		1.2	5.91	7.34
		1.6	7.92	
		2.0	10.60	
III	9.8	0.8	18.37	
IV	17.3	0.8	17.72	19.07
		1.2	19.30	
V	35.3	0.8		7.73
		1.6		12.38
		2.4		16.29
VI	53.1	0.8		3.12
		1.6		4.68
		2.4		6.14
VII	177˙	0.8		1.98
		1.6		2.41
		2.4		2.89
VIII	286	0.8		1.90
		1.6		2.20

In Tables VII and VIII are given the concentration ordinates at the end of a fixed time of multiple weights of each of the fractions of anhydrite and gypsum, respectively. From these values the relative specific rate of solution of the fractions taken in pairs was calculated, with results as shown in Tables IX and X.

TABLE IX

Relative Rate of Solution of Different Particle Size Fractions of Anhydrite added dry at a Stirring Speed of 130 r.p.m.

Fraction	Surface Mean Diameter	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor
I	1.10	1.72	.82	0.477	.32
II	1.89	3.12	.26	0.083	.68
III	5.9	2.49	4.31	1.73	8.14
IV	14.7	1.80	4.87	2.71	4.70
V	26.5	2.03	3.59	1.77	1.74
VI	53.8	2.93	3.34	1.14	0.98
VII	157	1.59	1.37	.86	0.86
VIII	250	1.00	1.00	1.00	1.00

TABLE X

Relative Rate of Solution of Different Particle Size Fractions of Gypsum added dry at a Stirring Speed of 130 r.p.m.

Fraction	Surface Mean Diameter microns	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor
I	1.10	2.92	1.02	.35	.07
II	3.22	3.04	.20	.067	.20
III	9.8	1.77	1.23	.69	3.00
IV	17.3	2.04	3.77	1.85	4.35
V	35.3	1.50	4.16	2.77	2.35
VI	53.1	3.33	3.53	1.06	0.85
VII	177	1.61	1.29	0.80	0.80
VIII	286	1.00	1.00	1.00	1.00

The dissolution factor shown in column 6 of Tables IX and X is obtained by setting the rate of solution of the coarsest fraction (VIII) equal to unity. It is, therefore, the relative specific rate of solution of each fraction referred to the coarsest as standard.

In Fig. 16, the dissolution factor for anhydrite at 130 r.p.m. is plotted from Table IX in comparison with the values previously obtained at 470 r.p.m.;[2] in Fig. 17 the values of the dissolution factor for gypsum at 130 r.p.m. are plotted from Table X in comparison with those for anhydrite at the same stirring speed.

Fig. 16

Relative Rate of Solution of
Different Particle Sizes of
Anhydrite at Different Stirring Speeds

Dissolution Factor
v.s.
Surface Mean Diameter

—— Anhydrite, 130 r.p.m.
----Anhydrite, 470 r.p.m.

Microns

Fig. 17

Relative Rate of Solution of
Different Particle Sizes of
Gypsum and Anhydrite at
the Same Stirring Speed

Dissolution Factor
v.s.
Surface Mean Diameter

—— Gypsum, 130 r.p.m.
-- Anhydrite, 130 r.p.m.

Microns

Considering from these figures the results for anhydrite and gypsum added dry at the same slow stirring speed of 130 r.p.m., it is seen that below 50 microns the dissolution factor is enhanced above the normal value unity and reaches a maximum. This maximum is for anhydrite 8.6 at a particle size of 7.0 microns. For gypsum the maximum is about half as great, 4.4, and is displaced to a coarser particle size of 16.5 microns. With decrease in particle size below the maximum, the dissolution factor reaches the normal value unity at 2.1 microns for anhydrite and at 5.1 microns for gypsum; thereafter with further decrease in particle size it diminishes to very low values. As already indicated the maximum in the dissolution factor and subsequent decrease are to be ascribed to the effect of mutual attraction and adherence of the grains when simply added dry to the solvent.

At the higher stirring speed, as shown in Fig. 16, the maximum for anhydrite is now 17.6 as against 8.6, and is displaced from 7.0 microns at slow stirring to a particle size of 2.8 microns. This shows the selective increase in the dissolution of the finest grains added dry by increase in stirring speed. For particles greater than 50 microns the specific rate of solution is close to the normal value unity. For fraction VII at about 150 microns the value is nevertheless distinctly less both for anhydrite and gypsum. This corresponds to the relatively high rate of solution of the coarsest fraction VIII with which VII was compared and for which the dissolution factor is unity as standard. Due to the small number of grains involved, the solute of fraction VIII did not completely cover the bottom of the beaker and this probably explains the somewhat high rate observed for this fraction compared to VII.

Rate for Anhydrite dispersed in Water

Since it had been found that initial dispersal of the fine grains of fraction II of anhydrite enormously increased the rate of solution at slow stirring, it was decided to run a series of experiments with the anhydrite powder initially dispersed, similar to that with the powder added dry.

Preliminary trial showed that the use of 3 c.c. of dispersing water gave the same rate of solution as 2 c.c., except for fraction I (1.10 microns). In this instance the amount dissolved after 6 minutes from 0.8 gram was 0.1915 grams $CaSO_4$/100 c.c. with 3 c.c. against 0.1686 grams per 100 c.c. with 2 c.c. Accordingly the larger quantity of dispersing water was used with this fraction and also, for the sake of uniformity, with fraction II (1.89 microns).

Correction of the measured concentrations was made for the amount dissolved in the 2 or 3 c.c. of dispersing water. It was found for all the fractions but VI that the dispersing water was saturated so that the correction was 0.0030 gram per c.c.[2] For 0.8 gram of fraction VI the water was three-fourths saturated. Runs were not made with the coarsest fractions VII and VIII because of the formation of an adherent sludge in the weighing tube.

The time-concentration values are shown in Table XI. Fig. 18 in which these results are plotted shows that the dissolution curves are of the same

form as for the anhydrite and gypsum added dry (Figs. 14 and 15). It is seen that the rate of solution of fractions I and II initially dispersed is enormously increased over that of the same solute added dry; the increase is considerably less for fraction III and but very slight for the coarser fractions.

Figure 16

Dissolution of Anhydrite Initially Dispersed in Water

0.8 gr per 100 cc of 130 r.p.m
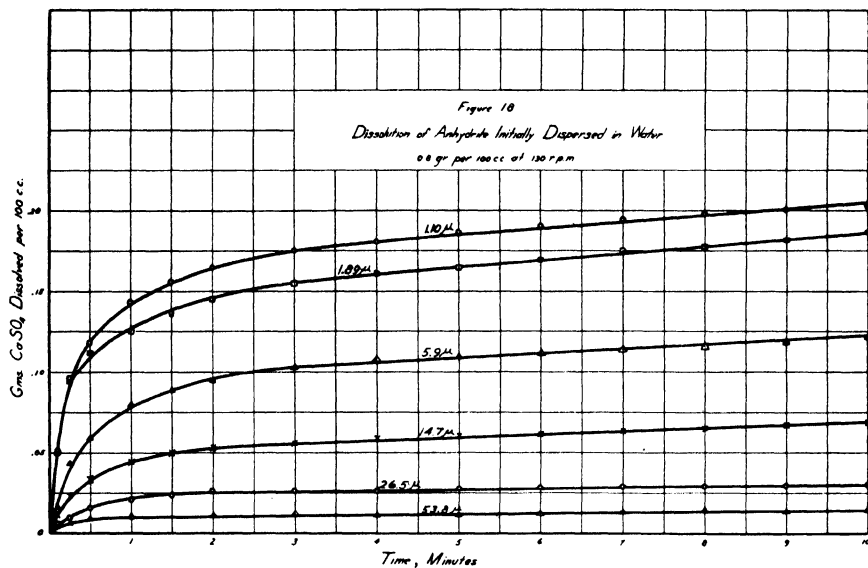
TABLE XI

Dissolution of 0.8 Gram Anhydrite, initially dispersed in Water, in 100 c.cm. of Water at 130 r.p.m.

Time Min.	I	II	III	IV	V	VI	Fraction
			Surface Mean Diameter				
	1.10	1.89	5.9	14.7	26.5	53.8	Microns
			Grams $CaSO_4 \times 10^2$/100 c.c.				
0.1	5.20	5.10	1.56	.95	.57	.00	
0.25	9.70	9.54	4.32	2.39	.98	.54	
0.50	11.77	11.17	5.94	3.33	1.56	.70	
1.00	14.30	12.50	8.00	4.40	2.17	.85	
1.5	15.62	13.65	8.81	5.00	2.42	.92	
2.0	16.46	14.50	9.49	5.33	2.58	.98	
3.0	17.50	15.50	10.30	5.67	2.61	1.02	
4.0	18.15	16.10	10.80	5.88	2.68	1.06	
5.0	18.76	16.53	11.00	6.06	2.76	1.09	
6.0	19.15	16.96	11.21	6.21	2.83	1.12	
7.0	19.40	17.50	11.40	6.40	2.91	1.16	
8.0	19.83	17.84	11.60	6.55	2.96	1.19	
9.0	20.05	18.17	11.82	6.80	3.00	1.22	
10.0	20.30	18.68	12.02	6.90	3.02	1.25	

Relative Rate of Solution versus Particle Size for Anhydrite dispersed

The method of determining the relative rate of solution of the different fractions is the same as that for the powder added dry. Table XII shows the concentration ordinates after 6 minutes of multiple weights of o.8 gram of each of the fractions. It is seen for 1.6 grams of fractions IV and V in contrast to the result for o.8 gram where the rates were practically the same, that the rate of solution with the powder dispersed is appreciably higher than for the same material added dry.

TABLE XII

Comparison of Concentration Ordinates for initially
dispersed Anhydrite at 130 r.p.m.

Fraction	Surface Mean Diameter	Grams taken for Solution	Dissolved, gr. $CaSO_4 \times 10^{-2}$ in 100 c.c. after 6 min.
I	1.10	0.8	19.15
II	1.89	0.8	16.96
		1.6	19.00
III	5.9	0.8	11.21
		1.6	12.68
		2.4	13.65
IV	14.7	0.8	6.21
		1.6	8.92
V	26.5	0.8	2.83
		1.6	4.45
VI	53.8	0.8	1.12
		1.6	1.74

TABLE XIII

Relative Rate of Solution of Different Particle Sizes of Anhydrite,
initially dispersed in Water, at 130 r.p.m.

Fraction	Surface Mean Diameter microns	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor	Dissolution Factor Dry
I	1.10	1.72	2.28	1.32	9.94	.33
II	1.89	3.12	6.26	2.01	7.51	.69
III	5.9	2.49	2.92	1.17	3.75	8.30
IV	14.7	1.80	3.12	1.73	3.21	4.80
V	26.5	2.03	3.84	1.85	1.85	1.77
VI	53.8	1.00	1.00	1.00	1.00	1.00

The specific rate of solution of the fractions taken in pairs, and from this the dissolution factor, were calculated as above with results shown in Table XIII. In this table a value of unity has been chosen for the dissolution factor of fraction VI which is closely justified from the results of Table IX. In the last column of Table XIII the dissolution factor for the anhydrite added dry is recalculated for purpose of comparison to a basis of unity for fraction VI. In Fig. 19 is a plot of the dissolution factor versus particle size for the anhydrite initially dispersed and added dry.

Fig 19
Relative Rate of Solution of
Different Particle Sizes of
Anhydrite added Dry and
After First Dispersing in
Water – Stirring Speed 130 r.p.m.
Dissolution Factor
v.s.
Surface Mean Diameter
—— Dispersed in Water
-- Dry

Microns
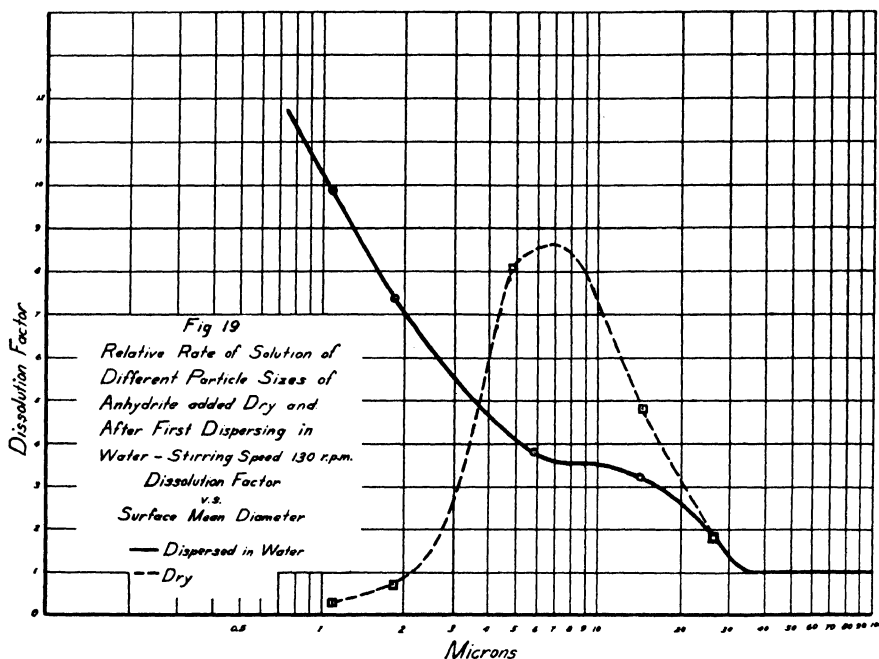
It is seen that for fraction V the dissolution factor is closely the same in both cases. For smaller particles it is less for the powder dispersed until a flat inflection point is reached that lies near the particle size corresponding to the maximum for the powder added dry, that is, at 8 microns. With further decrease in particle size beyond the inflection point, the dissolution factor increases continuously from 3.6 to a value of 7.2 at 2 microns and 10.2 at 1 micron.

Physical Interaction of the Microscopic Grains

It has been seen that the mutual attraction of the particles below about 5 microns hindered the action of the solvent so that the rate of solution of the solute added dry was inhibited. Indeed, with the 1.10 micron fraction of anhydrite, initial dispersal with violent shaking in 2 c.c. of water was not sufficient to detach the "associated" grains; a higher dilution by the use of 3 c.c. was necessary. The differences in dissolution factor of anhydrite fractions III and IV dispersed and dry suggests that a physical interaction

of the grains of some kind may also play a part for these less fine particles (5.90 and 14.7 microns). In particular it is to be noted that the difference in dissolution factor is due to the greater rate of solution, dispersed over dry, of 1.6 grams of each of the fractions IV and V (14.7 and 26.5 microns), although with 0.8 gram the rate was closely the same.

It has been seen that for all the fractions added dry, settling of the solute was complete in 5 seconds. Essentially then, solution for these fractions takes place from the sediment in contact with a stirred liquid. It is evident that the solvent penetrates to the interior of sediment and solution takes place therein. For if, on the contrary, the surface of the sediment alone dissolved, the rate of solution would be closely the same for all fractions of a given substance, especially in view of the results of Bruner and Tolloczko[25] and Brunner[6] that a rough pitted surface affected the rate of solution but little, that is, that the projected surface determined the rate. Secondly, it would be impossible to explain on any other basis than that solution takes place in the interior of the sediment, the fact that the concentration ordinate at a fixed time increases in the range of solute weights covered at the same rate as the increase in weight of solute taken for solution.

In view then, of the consideration that the solvent flows through the sediment, the structure of the latter, in so far as it may vary from fraction to fraction, will be an important variable in deciding the relative rate of solution. A loose structure will permit a more rapid flow of the solvent through the dissolving sediment than one densely packed; due to displacement and orientation of the particles[26] the contact between the solvent and individual grains also will be rendered more effective.

For coarse grains the specific volume of a settled powder is essentially independent of the particle size. On the other hand, for finer grains it is found that the sediment volume increases with decrease in particle size. For powders in air this has been found to be true for particles less than about 20 microns.[27] For a quartz powder in contact with an electrolyte, Buzágh[28] found that the sedimentation volume increased with decrease in particle size below about 100 microns. To see whether this was also true for the anhydrite fractions in question, the sedimentation volume was measured by shaking with 10 c.c. of water for 30 seconds and allowing to settle. In the case of fractions I and II, the volume was also determined after adding the powder dry to the water without shaking. Temperature was maintained constant in a forced-draft air bath at 22.0 ± .1°C. The measuring cylinder, graduated in 1/10 c.c., was 12.88 mm. in diameter, and was calibrated with mercury, correction being made for the meniscus. Readings were made with a magnifying lens at suitable time intervals.

The results which are the average of two or more measurements are shown in Table XIV.

[25] Bruner and Tolloczko: Z. physik. Chem., **35**, 283 (1900).

[26] Hatschek: J. Soc. Chem. Ind., **27**, 538 (1908).

[27] Roller: Ind. Eng. Chem., **22**, 1206 (1930).

[28] Buzágh: Kolloidchem. Beihefte, **32**, 114 (1930).

TABLE XIV

Sediment Volume of Anhydrite Fractions at 22°C.

Fraction	Surface Mean Diameter	Time, mins.				
		5	10	15	30	60
			Volume, c.c. per gram.			
VIII	250	.71	.70	.70	.70	.70
VII	157	.70	.70	.70	.70	.70
VI	53.8	.73	.73	.73	.73	.73
V	26.5	.80	.79	.79	.79	.79
IV	14.7	.88	.88	.88	.88	.88
III	5.9	1.46	1.14	1.07	.96	.96
II	1.89	9.34	8.32	7.21	4.16	3.40
I	1.10	9.43	8.04	6.88	5.55	4.83
II	1.89*	1.15	1.15	1.15	1.15	1.15
I	1.10*	1.35	1.35	1.35	1.35	1.35

* Added dry to water without shaking.

From this table sedimentation of the dispersed material is seen to be complete in 5 minutes for fractions IV to VII, in 15 minutes for fraction III, while for fractions I and II the volume is still decreasing after 60 minutes at the low rate of .02 c.c. per minute. For the same fractions I and II added dry, the end volume is reached in 5 minutes and is considerably less than for the material shaken up. Considering the end sedimentation volume, it is seen that this is constant above about 100 microns, but thereafter increases with decrease in particle size.

In explanation of this augmented effect below 100 microns (and also for the effect caused by a change in solvent or of electrolyte concentration) Ostwald and Haller[29] and Pawlow[30] assume that the particles are surrounded by a "solvate" layer that may vary in thickness. On the other hand, Ehrenberg[31] and Buzágh[28] incline to the view that increase in sediment volume is due to an increasingly loose structure, with contact of the grains at edges and corners resulting in ramifying aggregates. Usher[32] and McDowell and Usher[33] have recently obtained evidence that the latter interpretation is the correct one in contrast to the theory of the solvate layer.

An attempt was made to see what difference is effected in the structure of a sediment, as measured by the volume, by differences in the manner of adding the powder to the water. It was endeavored to simulate conditions that obtain in the actual rate of solution experiments with the solute added dry and initially dispersed. The final sedimentation volume was measured (a) with the powder added dry to the water in the measuring cylinder, (b) after shaking, and (c) after centrifuging. The results are shown in Table XV.

[29] Ostwald and Haller: Kolloidchem. Beihefte, 29, 354 (1929).
[30] Pawlow: Kolloid-Z., 42, 112 (1927).
[31] Ehrenberg: "Bodenkolloide," 83 (1918).
[32] Usher: Proc. Roy. Soc., 125A, 143 (1929).
[33] McDowell and Usher: Proc. Roy. Soc., 131A, 564 (1931).

TABLE XV

Sediment Volume of Anhydrite Fractions under Different Conditions
at 23-25°C.

| Fraction | Surface Mean Diameter | Volume, c.c. per gram | | |
		Added Dry	Shaken Up	Centrifuged
III	5.9	.89	.96	.66
IV	14.7	.75	.89	.69
V	26.5	.72	.81	.66
VI	53.8	.71	.71	.66
VII	157	.70	.72	.71

It is seen that the sedimentation volume of the powder added dry is intermediate between the values obtained by shaking and by centrifuging. In the last instance, a densely packed structure obtains as is seen by the fact that the volume after centrifuging is nearly the same for all fractions. For the coarsest fraction, the sedimentation volume is closely the same, regardless of the manner of adding the powder. In actual rate of solution measurements, differences in the sedimentation structure due to adding the solute dry or dispersed will, of course, be less than indicated in Table XV because of the dispersing effect of the stirrer.

In order to secure more information concerning the structure of the sediment, experiments were made on the time of filtration of 10 c.c. of water through the different fractions. The filter was of G-3 Jena fritted glass 14 mm. in diameter. The temperature was 24.5 ± .3°C. and the pressure was maintained constant at 15 cm. of mercury by a regulator similar to that described by Cox.[34]

In the instance of fractions IV and V, there was a steady increase in resistance with each successive 10 c.c. pass. The results for different weights of each fraction which are the average of about 6 successive passes, are shown in Table XVI.

TABLE XVI

Filtration of Anhydrite Fractions at 24.5 ± .3°C.
under a Head of 15 cms. Hg.

Fraction	Surface Mean Diameter	Weight Taken	Time of Outflow of 10 c.c. mins.
VII	157	0.5	51.6
		1.0	54.0
VI	53.8	0.5	77.2
		1.0	80.0
V	26.5	0.5	117
		1.0	142
		1.5	162
IV	14.7	0.5	301
		1.0	381

[34] Cox: Ind. Eng. Chem., Anal. Ed., 1, 7 (1929).

The resistance as measured by the time of outflow for 0.5 gram of powder, is due to both that of the powder itself and of the clogged filter. Consequently, it is the difference in resistance between 0.5 and 1.0 grams that corresponds to the resistance of the powder itself. The results show that this resistance increases rapidly with decrease in particle size below 53.8 microns.

It is to be noted that in the filtration experiments the final structure of the sediment was altered to a densely packed one by the pressure. If in the rate of solution measurements the flow of the solvent through the sediment corresponded to the filtration resistances of Table XVI, it is clear that the rate of solution would decrease rapidly with decrease in particle size instead of increasing as observed. It may be concluded, therefore, that the structure of the sediment as measured by the sediment volume of Tables XIV and XV is of fundamental importance in determining the relative rate of solution of the powder added dry.

This conclusion can be tested directly. It may reasonably be expected that, although the powder added dry has settled in 5 seconds, still for an appreciable time thereafter the physical interaction of the grains might alter so as to form a denser structure. If stirring of the solution be stopped now for a certain period, and then resumed, any increase in density of the structure would, during the quiescent period, in which the amount dissolved is negligible, be reflected in a decrease in the concentration at equal periods of stirring with respect to the normal uninterrupted procedure.

Eight-tenths gram of anhydrite fractions II, III, V, and VII were added dry to 100 c.c. of water in the usual manner. The normal procedure was varied, however, by stopping the stirring after 40 seconds for a period of about 6 minutes, and then resuming.

Because of other objectives that were contemplated, the measurements were carried out in a Pyrex beaker described above. Owing to the increased dimensions of the beaker the effectiveness of the stirring was decreased with a resultant decrease for all the fractions in the rate of solution with respect to that normally obtained. This was especially true for fraction III (5.9 microns) due to a large extent to the inability to effectively distribute the "lumped" fraction over the bottom of the beaker. In Table XVII, in which

TABLE XVII

Dissolution of 0.8 gr. Anhydrite added dry to 100 c.c. Water,
Continuous and Interrupted Stirring

Fraction	Particle Size Fraction microns	Grams $CaSO_4 \times 10^2/100$ c.c. after 6 minutes of Stirring	
		Continuous Stirring	Interrupted Stirring
II	1.89	4.41	4.50
III	5.9	5.80	4.48
V	26.5	1.66	1.62
VII	157	.59	.72

the results obtained are recorded, it is seen that for fractions II and VII, corresponding to a permanently structured sediment, the concentration after 6 minutes of interrupted stirring is slightly greater, as would normally be expected, than for 6 minutes of continuous stirring. On the other hand, with fractions III and V, the converse is true well within the experimental error. The unusual result for these fractions is to be interpreted as due to the increasing density of the sediment structure during the 6-minute quiescent period. This effect results in a subsequent decrease in the rate of solution which more than compensates for the slight amount of solution during the period of nonstirring.

In light of the above evidence and conclusions, the difference in the dissolution factor of anhydrite fractions III and IV when dispersed and added dry, is due to a more loosely structured sediment of the 1.6 grams of solute of the comparison fractions IV and V when initially dispersed in water. Indeed it may be concluded that the physical interaction of the grains, varying with particle size below about 50 microns and with experimental conditions, is, for the powder added dry, the most important factor in determining the relative rate of solution as a function of size of grain.

Non-existence of Theoretical Nernst Film

It has been seen that all the fractions added dry dissolve as a sediment through which the solvent flows during stirring. This means that the solvent actively penetrates to a point near the surface of the grains, that is, to at least one-half the mean distance of separation of the particles. Assuming these to be cubes, the mean half-distance of separation may be calculated from the following easily derived equation:

$$(2) \quad 3\tau/d + 6 \ (\tau/d)^2 + 4(\tau/d)^3 = \rho V/2$$

where d is the length of a cube edge (average particle diameter), τ the mean distance of separation, ρ the density, and V the volume of the sediment per gram.

From the values of Table XIV calculations of the half-distance of separation of the grains have been made by the use of equation (2) with results shown in Table XVIII. It is seen that $\tau/2$ which is only 17.5 microns for the

TABLE XVIII

Mean Distance of Separation of Grains of Anhydrite

Fraction	Surface Mean Diameter	Sedimentation Volume V, c.c. per gram	Mean Distance τ, microns
VII	157	.70	35
VI	53.8	.73	12
V	26.5	.79	6.5
IV	14.7	.88	3.9
III	5.9	.96	1.6
II	1.89	1.15	.60
I	1.10	1.35	.39

coarsest fraction VII rapidly decreases to a value of .19 microns for fraction I. That the solvent actively penetrated the latter sediment is seen from the fact that increasing weights of this solute resulted in proportionate increases in the rate of solution. Consequently, the theoretical Nernst film, if it exists, must be smaller than 0.2 micron, a value that is less than 1/100 of that calculated from the Nernst diffusion film theory, 20 to 50 microns.

Spangenberg[35] found by observation under the microscope that the slightest disturbance of a saturated solution in contact with a crystal of NaCl was communicated within about 0.4 micron, the resolving power of the microscope, which is far within the 20 to 50 micron range of the Nernst film. Recent careful measurements by Bulkley[36] of flow through capillary tubes show that motion of the fluid exists at least as close as 0.03 micron from the surface for a flow as small as 1/400,000 c.c. per minute. Miyamoto, Kaya, and Nakata[37] found that a monomolecular film of palmitic and stearic acids barely affected the rate of oxidation of sodium sulphite solution by O_2, and concluded "that the thickness of the stationary film, if it exists, should be smaller than 23.7×10^{-8} cm."

In agreement with the result found in this work, independent and direct evidence strongly contradicts the existence of the theoretical Nernst diffusion film. Apparently then, the enhanced rate of solution with decrease in particle size that has been observed can in no way be attributed to a decrease in thickness of such a film with decrease in particle size.

Effect of Edges and Corners

There is increasing evidence that catalysis, solution and crystallization take place at "active centers" which may be "crystal defects," edges, and corners.[13,14,15,16,17,18] The number of edges per gram increases inversely as the square of the particle size, and the number of corners inversely as the cube.[19] Therefore, if the edges and corners alone were active, one should expect the rate of solution to be inversely proportional, not to the first power of the particle size as would ordinarily be expected, but to the second and third power, respectively. In general, however, the surface may be expected to play a part, and therefore the effect of edges and corners would be apparent only below a certain particle size and the exponent would then fall between 1 and 3.

From Tables IX, X and XIII in which are given the relative rate of solution of the fractions taken in pairs at 130 r.p.m. and also, from results previously obtained at 470 r.p.m.,[2] the exponent n in the equation:

$$(3) \quad R_1/R_2 = (S_1/S_2)^n$$

has been calculated for the fractions taken in pairs. In equation (3) R_1/R_2 is the relative rate of solution, S_1/S_2 the relative surface per gram of two adjacent fractions.

[35] Spangenberg: Z. Krist., **59**, 383 (1923).

[36] Bulkley: Bureau Standards, J. Res., **6**, 89 (1931).

[37] Miyamoto, Kaya, and Nakata: Bull. Chem. Soc. Japan, **6**, 133 (1931).

It is seen from Table XIX that for the fractions added dry the calculated values of n are quite variable, lying above 3 in two cases and below 0 for fractions I and II of anhydrite and II of gypsum at slow stirring. In view of all the considerations that have been advanced, the values of n for the solute added dry obviously depend essentially on the structure of the sediment and not on the effect of corners and edges.

TABLE XIX

Value of Exponent n for Fractions taken in Pairs

| Fraction | Anhydrite | | | Gypsum |
	Added dry 130 r.p.m.	Added dry 470 r.p.m.	Initially dispersed 130 r.p.m.	Added dry 130 r.p.m.
I	− .36	1.10	1.51	.018
II	−1.18	1.95	1.62	− .60
III	1.60	3.13	1.17	.36
IV	2.70	2.10	1.93	1.86
V	1.81	1.03	1.90	3.52
VI	1.12			1.05
VII	.68			.54

However, for the solute initially dispersed in water the situation is different. Fractions I and II of anhydrite (1.10 and 1.89 microns) throughout the experiment remained suspended in the solvent. The slight settling effect of the first 10 minutes is quite similar for both fractions as seen from Table XIV. Fractions III and IV (5.9 and 14.7 microns) are still partially suspended in the solution after the first two or three minutes. On pouring the solution out of the beaker after several minutes of stirring, the solute flows out with it as though it were thoroughly suspended. On the other hand, fractions V and VI (26.5 and 53.8 microns) have completely settled in 1½ and ½ minutes, respectively; and on pouring out the solution, these grains in contrast to the particles of fractions I to IV tend to adhere to themselves and to the beaker in the manner of coarse sand. It is reasonable to conclude that for these coarser fractions the structure of the sediment strongly influences the relative rate of solution; on the other hand, for fractions I, II, III, and IV, (1.10 to 14.7 microns) initially dispersed in water, the physical interaction of the grains due to their effective separation is negligible or nil and the rate of solution corresponds to the activity of the individual particles.

This conclusion appears to be substantiated by the results shown in Fig. 19 for anhydrite dispersed. At 8 microns there is a flat inflection point at which the rate of change of the dissolution factor with particle size is nil; in other words, at this particular point the rate of solution is, by definition of the dissolution factor, strictly proportional to the surface exposed. This can be accounted for by the fact that owing to the effective dispersion of the fine grains corresponding to the inflection point, their physical interaction has vanished and no longer affects the rate of solution with decrease in particle size.

For coarser particles below 8 microns and up to 50 microns, the physical interaction, decreasing with diminution of particle size, results in an increase in the dissolution factor as observed.

For the particles less than 8 microns, there is again an increase in the dissolution factor. Since the physical interaction no longer plays a part here, the enhanced rate of solution must correspond solely to the effect of edges and corners.

The edges E, and corners C, per sq. cm. can be determined from the statistical count of Table I by equations similar to that of (1) for the surface mean diameter. We have

$$(4) \quad E = 2\Sigma d/ \Sigma d^2$$

$$(5) \quad C = 1.33 \ 1/\Sigma d^2$$

In Table XX are given the results of calculation of n, E, and C. n is recalculated from Table XIII for fractions I, II, and III of anhydrite to a particle size of 8 microns as standard. It is seen that corresponding exclusively to the effect of edges and corners on the rate of solution, n is above unity for fraction III (5.9 microns) and substantially so for fractions II and I lying below 2 microns. The uncertainty in n can be calculated from the individual measurements and is ±.09, ±.06, and ±.11 for fractions III, II, and I, respectively.

<h3 style="text-align:center">TABLE XX</h3>

<p style="text-align:center">Value of Exponent n for Anhydrite, initially dispersed,
Referred to 8 micron Particle as Standard</p>

Fraction	Surface Mean Diameter microns	Edges per Unit Surface microns^{-1}	Corners per Unit Surface microns^{-2}	n
I	1.10	2.22	1.80	1.51
II	1.89	1.94	1.48	1.51
III	5.9	.40	.06	1.13
IV	8.0	.25	.02	1.00

Since n in Table XX is appreciably less than 2, the value corresponding to solution solely by way of the edges, and from the fact that the dissolution factor is close to unity for the coarse fractions VI, VII, and VIII, it appears that solution of the anhydrite takes place directly at the surface as well as by way of the edges.

However, to account for the observed appreciable effect of the edges (and corners), it is necessary to conclude that solution at the surface of the anhydrite takes place not uniformly but via the active centers. This conclusion comes about from the fact that even for a 1-micron particle the proportion of edge to surface atoms is slight, about 10^{-3}, and is thus insufficient to account for a value of n as high as 1.5; however, the proportion is quite appreciable with respect to the active centers since from the work of Smekal[14] the concentration of these is of about the same order.

Summary

1. A finely ground crystalline anhydrite and gypsum powder were separated into homogeneous particle size fractions between 1 and 250 microns surface mean diameter. The relative rate of solution of these fractions in water was determined by conductivity measurement at 20°C. at a stirring speed of 130 r.p.m.

The time concentration curves are of the same form for all the fractions. There is an initial high rate of solution that decreases rapidly in the first 2 or 3 minutes to a slow almost linear rate. For the finest fractions up to about 17 microns, added dry to the solvent, there is a slight induction period of 4 or 5 seconds.

2. With the solute added dry to the solvent at the slow stirring speed, the rate of solution of the fractions below 5 microns of both anhydrite and gypsum is unexpectedly low. This is attributed to difficulty of penetration by the solvent to the individual grains of the solute due to their initial strong mutual attraction. In accordance with the greater softness of gypsum, the effect for this substance is more pronounced than for the anhydrite. Increase in speed of stirring (from 130 to 470 r.p.m.) selectively promotes the rate of solution of the finest particles below 5 microns to a value approaching normal.

It is shown that the inertness of the finest particles when added dry at slow stirring is not due to any appreciable extent to entrained air.

3. When the anhydrite solute is first dispersed in 2 or 3 cc. of water before adding to the solvent, the rate of solution of the finest particles below 5 microns is enormously increased. This is true to a lesser extent for the 5.9 micron fraction; for the coarser fractions up to 50 microns the rate is almost the same for the powder dispersed and dry. However, when the quantity of solute is increased from 0.8 to 1.6 grams, the rate of solution is here also greater dispersed than dry.

4. With the solute added dry, the dissolution factor, or the relative specific rate of solution referred to the coarsest fraction as unity, increases from unity to a maximum with decrease in particle size. At 130 r.p.m., the maximum for anhydrite has a value of 8.6 at 7.0 microns, as against 17.6 at 2.8 microns with a stirring speed of 470 r.p.m. With gypsum at 130 r.p.m., the maximum is only 4.4 at 16.5 microns. With decrease in particle size below the maximum, the dissolution factor falls below the normal value unity both for anhydrite and gypsum, but to a greater degree for the latter, at the same slow stirring.

5. With the anhydrite initially dispersed in 2 or 3 c.c. of water, the dissolution factor at a stirring speed of 130 r.p.m. increases above unity with decrease in particle size below about 50 microns, passing through a flat inflection point with the value of 3.6 at particle size of 8 microns; thereafter, the dissolution factor increases with decrease in particle size, reaching a value of 7.2 at 2 microns and 10.2 at 1 micron.

6. For all the fractions added dry, solution takes place essentially from a settled sediment through which the solvent flows. Evidence based upon measurement of sedimentation volume, rate of filtration, and rate of solution with interrupted stirring, is presented to show that the structure of the sediment, that is, whether loosely aggregated or densely packed, is most important in determining the rate of solution. The structure of the sediment depends on particle size below 100 microns and on conditions of experiment.

7. Quite apart from considerations which may be mentioned against the general Nernst diffusion theory of heterogeneous reaction, it is shown that the Nernst diffusion film, if it exists, must be smaller than 0.2 micron, or less than 1/100 of the theoretical value 20 to 50 microns. Direct evidence from recent literature is adduced to show still further that any film which may exist approaches molecular dimensions. Consequently, the assumption of a diffusion film appears to be invalid, and it is not possible to account for the observed enhanced rate of solution on the basis of a decrease in thickness of such an adherent film with decrease in particle size below 50 microns.

8. The experimental results are examined in light of the theory that solution takes place from active centers which involve the edges and corners of a crystal. For the solute added dry the structure of the sediment overcomes all other effects in determining the rate of solution. For the solute (anhydrite) initially dispersed, it appears that the same situation holds for particles greater than corresponds to the inflection point at 8 microns. Between this particle size and 50 microns the enhanced rate of solution is due to increasing dispersity of the solute with decrease in particle size. At 8 microns, the physical interaction of the grains vanishes and the rate of solution is proportional to the surface exposed. Below 8 microns the enhanced rate of solution is to be attributed solely to the effect of edges and corners. Taking the rate of solution proportional to the nth power of the surface exposed and referring to an 8-micron particle as standard, n is $1.13 \pm .09$ at a surface mean diameter of 5.9 microns, $1.51 \pm .06$ at a mean diameter of 1.89 microns, and $1.51 \pm .11$ at a mean diameter of 1.10 microns. Since the exponent is substantially less than 2 which would correspond to solution by way of the edges alone, the anhydrite crystals dissolve also at the surface. This confirms the conclusion derived from the fact that the dissolution factor is close to unity for the coarsest fractions. However, in order to account for the appreciable effect due to the edges and corners for particles between 1 and 8 microns, it is necessary to conclude that solution of the anhydrite at the surface is not uniform but is determined by active centers.

THE SOLUBILITY OF UREA IN WATER*

BY LOUIS SHNIDMAN AND ARTHUR A. SUNIER

Introduction

Although the solubility of urea in water has been the subject of several researches,[1,2,3] the precision of measurement in most cases is poor, and judging from the procedures used, the accuracy of the results may well be questioned. One purpose of the present research was, therefore, to attempt to determine more precisely and accurately the solubility of urea in water. The data are also of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

Materials

In work of this nature the materials used become of prime importance. Urea from two sources was used. First, the C. P. Grade of Baker's urea which was imported from Germany and made by the Synthetic Ammonia Carbon Dioxide Process[4] was used. It is interesting to note that at the present time apparently no urea is being made in the United States, all being imported from Germany. This sample of urea as received showed a melting point of 132.5°, but some solid insoluble material seemed to be present, so the urea was twice re-crystallized from distilled water. During the re-crystallization the temperature was never allowed to exceed 65°. The urea was then carefully dried at 55°C. in an electric oven for sixteen hours, after which the melting point was run. The melting point of the resulting crystals was 132.7°, which agrees exactly with the value of 132.7° recorded in the literature.[5]

Another sample of urea made from Calcium Cyanamid was used. This sample obtained through the courtesy of the Union Carbide Company, was made by them from Calcium Cyanamid in an experimental plant in 1925, and showed the following analysis:

Dry Basis

% Total Nitrogen	43.80		
Urea Nitrogen	40.40	Urea	86.62
Dicy Nitrogen	.18	Dicy	.27
Guanylurea Nitrogen	1.85	Guanylurea	3.37
Cyanamid Nitrogen	.18	Cyanamid	.27
Ammonia Nitrogen	.87	Ammonia	1.06
Insoluble Nitrogen	.13		
Combined H_2SO_4	5.52		
Moisture as received	7.35		

This sample although impure was re-crystallized carefully four times from distilled water and twice from Baker's C. P. Methanol. During the re-crystallization, the temperature never exceeded 65°. The final crystals from the second methanol re-crystallization were dried in an electric oven at 52° for 24 hours. The melting point of the resulting crystals was 132.6° which agrees closely with the value recorded in the literature. The melting point was taken as the prime criterion for the purity of the substances used. Thus, two samples of urea from different sources, originally made by different methods, were obtained in a high state of purity.

Procedure and Apparatus

The synthetic method of Alexejew[6] was employed in making the solubility determinations. This method consisted in heating weighed quantities of solvent and solute in a sealed tube, shaken in a water bath, and noting the temperature at which the solid phase had nearly disappeared. In recent years other investigators[7,8,9] have found this method to be an accurate and a reliable means for determining the solubility of solids in various solvents. As pointed out by these investigators, care must be taken in attaining true equilibrium conditions at the solubility temperature; this can ordinarily be obtained through slow heating. The apparatus used has been described earlier.[9] A temperature rise of 0.01° per minute was used in some cases, though in many cases thermostating for a period of time was employed. Sunier[9] pointed out that with a rate of heating of 0.01° per minute, results well within 0.1° of the true solubility temperature were obtained for naphthalene—aliphatic alcohol systems. The authors feel that this same degree of accuracy would hold for the urea-water system.

In the preparation of the sealed tubes for a run, precautions were taken to insure the presence of small crystals. Other investigators[7,8,9] have shown that the size of the crystal is of importance in attaining true equilibrium conditions. The method was that ordinarily employed and consisted in rapidly heating the tube to a temperature where all the solute dissolved, and then cooling rapidly with vigorous shaking.

Thin-wall pyrex tubes of seven millimeters internal diameter and approximately fourteen centimeters long were used. The tubes were cleaned with sulphuric-chromic acid cleaning solution, rinsed with distilled water, and then heated over an open Bunsen burner to dull redness, placed in a desiccator, allowed to cool, and weighed. In these determinations a thermometer certified by the Bureau of Standards was employed. The thermometer could be read to ±0.01° with the aid of a magnifying glass. The temperatures recorded should be accurate to ±0.02°.

Statements are found in the literature[1,10,11] to the effect that care is necessary in heating solutions of urea because of the danger of decomposition at higher temperatures. In order to study this point more clearly, and at the same time check the accuracy of the results obtained at higher temperatures, a tube originally showing a corrected solubility temperature of 73.11° was

heated to the temperature of boiling water (99°) with constant shaking for varying periods of time. The solubility temperature was re-determined after each period. The results are given in Table I, and are plotted in Fig. 1.

TABLE I

Effect of Heating at 99° on Solubility Temperature of Urea

Hrs. @ 99°	Solubility Temperature	Difference in degrees
0	73.11	—
1	73.08	−0.03
5	72.48	−0.63
10	71.36	−1.75
20	69.67	−3.44
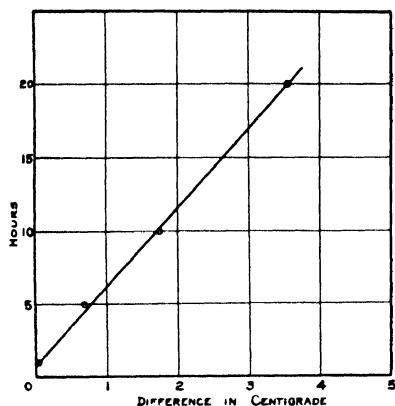
FIG. 1

Change in Solubility Temperature of Urea on Heating.

As shown above after one hour heating and shaking at 99°, a change of 0.03° was noticed. This change is probably within the degree of accuracy of the method at that temperature. Hence, it is concluded that the solubility temperatures in the higher range are accurate and are not affected by any decomposition, because at no time was the tube subjected to its solubility temperature for more than one hour, and then considerably below 99°. If little or no decomposition took place at 99° after one hour, it was quite certain that the change or decomposition taking place at temperatures of 73° or below would be negligible for periods of one or two hours.

Fig. 1 shows clearly that the rate of decomposition after the first hour and during the next nineteen hours of heating and shaking at 99°, as indicated by its solubility temperature, is a straight line function. It is of course quite possible that the presence of the ammonium cyanate produced, affects the solubility temperature to some extent; hence the solubility temperatures do not give a true indication of the amount or rate of decomposition. Walker[10] heated a decinormal urea solution at 100° and found that the transformation of urea into ammonium cyanate had reached equilibrium after one hour. The tube used for the above heating at 99° was approximately a 57.5 normal urea. It may be that the more concentrated solution shows a slower rate of transformation, which would explain the progressive lowering of the solubility temperature during the 20 hour heating period.

Results

The results of the various solubility determinations are presented in Tables II and III. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data was plotted on a large scale according to the method of Hildebrand and Jenks,[12] as the log N_2 vs. 1000/T. The solubilities at rounded temperatures were read off and are given in Table IV.

TABLE II

Solubility of Urea in Water

Urea made by Snythetic $NH_3 + CO_2$ Process (re-crystallized from water)

Grams Urea	Grams Solvent	Wgt. % Urea	Mol Fract. Urea	Solub. Temp.
1.5140	1.4486	51.10	0.2387	18.72
1.7891	1.4420	55.37	0.2712	26.83
1.8899	1.4951	55.83	0.2749	27.31
1.5119	1.0103	59.94	0.3099	35.42
2.3267	1.4955	60.87	0.3182	37.36
1.8298	1.0205	64.19	0.3498	43.94
2.8030	1.4832	65.39	0.3618	46.56
2.2347	0.9884	69.33	0.4041	54.77
2.1987	0.9250	70.38	0.4163	57.02
2.5702	0.9703	72.59	0.4428	61.76
2.3602	0.6823	77.57	0.5093	73.11

TABLE III

Solubility of Urea in Water

Urea made from Calcium Cyanamid—re-crystallized from water and methanol

Grams Urea	Grams Solvent	Wgt. % Urea	Mol Fract. Urea	Solub. Temp.
1.1217	1.0027	52.80	0.2513	21.59
1.7794	1.5176	53.97	0.2602	23.85
2.0496	1.5140	57.51	0.2888	30.38
1.5155	1.0114	59.97	0.3102	35.15
1.6631	0.9788	62.95	0.3377	41.11
1.8291	1.0148	64.31	0.3510	43.85
1.1159	0.4888	69.53	0.4065	54.97
2.2329	0.9520	70.10	0.4130	55.88
1.8579	0.7406	71.49	0.4294	59.13
1.3635	0.4879	73.64	0.4561	63.79
2.4081	0.7355	76.60	0.4956	70.49

TABLE IV

Solubility of Urea in Water at Rounded Temperatures
(expressed in Mol Fractions of Urea)

Temp. °C.	Synthetic Process N_2 Urea	Cynamid N_2 Urea	Mean N_2 Urea
20	0.2435	0.2447	0.2441
25	0.2642	0.2655	0.2649
30	0.2855	0.2868	0.2862
35	0.3080	0.3093	0.3086
40	0.3308	0.3322	0.3315
45	0.3554	0.3569	0.3561
50	0.3802	0.3816	0.3809
55	0.4060	0.4079	0.4069
60	0.4332	0.4349	0.4340
65	0.4609	0.4627	0.4618
70	0.4905	0.4920	0.4914

Discussion of Results

The results of these determinations were compared with those published by earlier workers. Speyers,[1] many years ago, determined the solubility of urea in water. He used Kahlbaum's urea (no doubt made from cyanamid), re-crystallized from ethyl alcohol, and dried on a steam radiator to prevent decomposition. Ordinary distilled water was used in these determinations. He used a thermometer said to be accurate to a tenth of a degree, and kept the solution at a temperature to within a tenth of a degree for ten minutes, and then analyzed the filtrate by the Kjehldahl distillation method. He states that the filtration was carried on while the temperature was cooling slightly. Speyers' results were not very precise, and a study of his method of attaining equilibrium and analyzing his samples leads to conclusion that the results are not very accurate. Krummacher[2] determined the solubility of urea, re-crystallized from ethyl alcohol, at the three temperatures, viz. 5.5, 17.1, and 20.92°C. His results at the two higher temperatures are in essential agreement with the results presented in this paper. Comparison at the lower temperature is not possible, except by a considerable extrapolation of the present curve. Pinck and Kelley[3] more recently determined the solubility of urea in water and found that at higher temperatures there was a marked deviation from the results published by Speyers. Their method consisted in heating from three to four hundred cc. of solution in a water bath in the presence of solid urea at a temperature a few degrees above that at which the solubility was determined. When the solution was cooled to the desired temperature, and after being maintained at this point for about ten minutes, a sample of twenty-five to thirty-five grams was taken. The dissolved urea was determined by the urease method of Fox and Geldard.[13] These authors used a sample of synthetic urea purified by two re-crystallizations from water. Their procedure in obtaining equilibrium was not of

extreme accuracy. Some of their results agree closely with the authors' determinations, but some of them, e.g. at the lower and higher temperatures, show some variations. The results of the above mentioned investigators are compared in graphic form with the authors' work in Fig. 2.

When Speyers' data are plotted according to the method of Hildebrand and Jenks,[12] no smooth or straight line curve results. When Pinck and Kelley's data are plotted in a similar manner, the curve also is not smooth. This deviation from the straight-line function was undoubtedly partly due to their method of obtaining equilibrium. The present data on the solubility
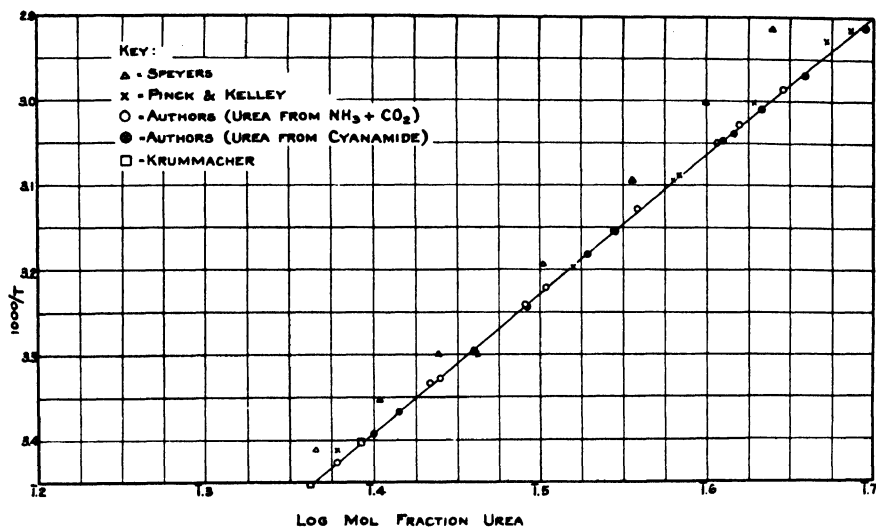
FIG. 2
Solubility of Urea in Water.

of urea made by two independent methods, plotted according to the method of Hildebrand and Jenks, yield a smooth and straight line curve. The results on the two samples of urea are so close that they overlap in many cases.

A study of Tables II and III shows the deviation obtained relative to the solubility of urea and water in two samples of urea made from different sources, and re-crystallized from water and methanol respectively. The fact that urea made by the synthetic method and urea made from calcium cyanamid shows such close agreement in regard to their solubility in water, leads to the conclusion that these determinations are more accurate than those of previously published work. This appears more plausible when it is recalled that the urea made by the synthetic process was re-crystallized from water, while that made from calcium cyanamid was re-crystallized from methanol. Hence, samples of urea made by two independent methods, and re-crystallized from water and methanol respectively, show close agreement as regards their solubility in water. These relations are brought out very clearly in Fig. 2. It is felt that the foregoing results are accurate to well

within $\pm 0.15°$ of the true solubility temperature; this figure representing the maximum deviation, whereas most of the determinations deviate much less. The mean deviation in the solubility temperature for the synthetic urea sample was $0.10°$, while for urea from calcium cyanamid it was $0.07°$. It is believed that the solubility results obtained with the sample of synthetic urea are nearer the true value, than those of urea from calcium cyanamid; first, because the former showed a slightly higher melting point, and secondly the product before re-crystallization was in a higher state of purity. However, in the final results (see Table IV) a mean value of the solubility of urea at rounded temperatures is presented. This mean value, representing the average of the solubilities of the respective samples of urea, was read off from the large plot, previously referred to. From this plot the equation of the mean straight line was determined and found to be $\log_{10}N = -609.8$ $(1/T) + 1.468$ and is valid over the temperature range $20°$ to $70°$ studied. It gives results to within one part per thousand of the values as obtained from the plot. Some nine preliminary determinations by Mr. E. Doell in this laboratory, using urea twice re-crystallized from absolute ethanol, has given results which lead to the same conclusion.

The fact that the log N vs. $1/T$ curve is a straight line, leads one to inquire whether or not ideal solutions are encountered in this range of concentration and temperature. When the curve is extrapolated to log $N = 0$, the intercept on the temperature axis gives a value of $142°$ whereas the melting point of pure urea is agreed to be $132.7°$. This discrepancy rather definitely points to the fact that the solutions are non-ideal, perhaps yielding a reverse S form of curve discussed by Mortimer.[14] No data seems to be available concerning

TABLE V

Vapor Pressure of Urea Solutions at $60.28°$
(Perman and Lovett's Data)

Mols Urea per Mol H_2O	Mol. Fract. Urea (Exp.)	Observed Vap. Press. (mm.)	Mol Fract. (Calc.)	% Diff. or Error
—	—	151.42	—	—
.0231	.0226	149.1	.0153	47.6
.0445	.0426	146.8	.0305	39.7
.0690	.0645	144.7	.0444	45.4
.0813	.0752	142.2	.0609	23.5
.1339	.1181	136.1	.1012	16.7
.1763	.1499	131.3	.1329	12.8
.2537	.2024	123.8	.1824	10.9
.3409	.2542	118.0	.2207	15.2
.4160	.2938	111.7	.2623	12.0
.4712	.3203	107.0	.2934	9.2
.5188	.3416	104.0	.3132	9.1
.6482	.3933	95.4	.3700	6.3
.8127	.4483	85.5	.4353	3.0

the latent heat of fusion of urea (no doubt because of the decomposition of urea at its melting point); hence a comparison of the experimental and ideal slope of the line is not possible. It may be said that when the slope, 609.8, is multiplied by 4.583, a value of approximately 2800 calories is obtained; if the solutions were ideal, this value would represent the molal latent heat of fusion of urea.

At least two sets of data are to be found in the literature dealing with the vapor pressures of urea solutions. That of Perman and Lovett[15] covers quite a range of concentrations at several temperatures. Since these authors did not present any calculations of deviations from Raoult's law (Bancroft[16] in a recent article mentions briefly the variation of these data from Raoult's law) calculations have been made using their data. The pertinent data and the results of the calculations at only one temperature — 60.28° would appear to be of sufficient interest to be included in this paper.

In Table V columns one and three are taken directly from the paper of Perman and Lovett. In column two concentrations are recorded on the mol fraction basis. Column four gives the mol fractions calculated by substituting the proper values in the well known equation $(p_0 - p)/p_0 = x$ of Raoult. The difference between the experimental and calculated values of the mol fraction is seen to vary from nearly 50 per cent to 3 per cent. Similar calculations using Perman and Lovett's data at 40.02° where the mol fraction of urea ranged from 0.0595 to 0.4021 showed a deviation from Raoult's Law decreasing from nearly 40 per cent to 8 per cent; the data at 80.10° where the mol fraction of urea ranged from 0.0431 to 0.5547 showed deviations from Raoult's Law decreasing from nearly 180 per cent to 1 per cent. One peculiar point is worthy of mention, viz. the deviations are greatest in the most dilute solutions in all cases. This may in part be explained by the relatively small pressure differences encountered at the lower concentrations, but it is hardly possible that this explanation holds throughout the range of concentrations studied. It would appear that with solutions of most other substances studied, the deviations from Raoult's Law are greater in the more concentrated solutions. An example of this is found in the work of Berkeley, Hartley, and Burton[17] on the vapor pressures of sugar solutions. These workers have found that on increasing the mol fraction of sugar from 0.0175 to 0.1025, the deviation from Raoult's Law increases from 10 per cent to 37 per cent. Such results, along with others which are not presented at this time, lead one to the view that any attempt to express quantitatively the deviations from Raoult's Law for urea solutions should be postponed until further data are accumulated. The data of R. Fricke[18] on the vapor pressure of urea solutions were obtained at temperatures near zero degrees centigrade and are confined to only three concentrations at two different temperatures, and thus do not materially assist in deciding the question just touched upon. In connection with the work of Perman and Lovett, it may be well to mention further that some of the more concentrated solutions were super-saturated, a fact apparently known to the authors when the work was under way.

As a result of their study of the heat of solution and heat of dilution curves of urea solutions, Perman and Lovett[15] have suggested a new method of determining solubilities, viz. "If a number of points of the Heat of Solution curve were determined and afterwards a number on the Heat of Dilution curve, it is obvious that these curves would intersect at the saturation point and would indicate the solubility of the substance." The results so obtained for urea solutions differ by about 1.4 per cent by weight at 50°. It may be said that Perman and Lovett did not claim a high precision for the solubility determined in this way.

Summary

1. Samples of urea from two different sources have been carefully purified.

2. Some twenty-two determinations of the solubility of urea in water have been made using the synthetic method in the temperature interval 20° to 70°; the precision of measurement in these runs is much higher than any previously published; it is believed that this is true of the accuracy also. The data may be accurately represented by the following equation, $\log_{10}N = -609.8\,(1/T) + 1.468$.

3. Preliminary data are presented showing the effect of varying periods of heating on the solubility temperature.

Literature cited

[1] Speyers: Am. J. Sci., (4) **14**, 294 (1902).

[2] Krummacher: Z. Biol., **46**, 302 (1905).

[3] Pinck and Kelley: J. Am. Chem. Soc., **47**, 2170 (1925).

[4] Bosch and Merser: U. S. Patent—1,429,483 (Sept. 19, 1922).

[5] Inter. Crit. Tables, **1**, 177.

[6] Wied. Ann., **28**, 305 (1886).

[7] Ward: J. Phys. Chem., **30**, 1316 (1926).

[8] Sunier and Rosenblum: J. Phys. Chem., **32**, 1049 (1928).

[9] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[10] Walker: J. Chem. Soc., **67**, 746 (1895).

[11] Thorpe: "Dictionary of Applied Chemistry," **7**, 271 (1927).

[12] Hildebrand and Jenks: J. Am. Chem. Soc., **42**, 2180 (1920).

[13] Fox and Geldard: Ind. Eng. Chem., **15**, 743 (1923).

[14] Mortimer: J. Am. Chem. Soc., **44**, 1416 (1922); **45**, 633 (1923).

[15] Perman and Lovett: Trans. Faraday Soc., **22**, 1 (1926).

[16] Bancroft: J. Phys. Chem., **35**, 3160 (1931).

[17] Phil. Trans. Roy. Soc., **218A**, 295 (1919).

[18] R. Fricke: Z. Elektrochemie, **35**, 631-40 (1929).

ADSORPTION OF THORIUM X BY FERRIC HYDROXIDE
AT DIFFERENT pH

BY IW. KURBATOW

The Properties and the Methods of obtaining highly Emanating Preparations

Hydroxides of different elements containing radium or thorium X uniformly distributed throughout their entire mass are able to give off quantitatively emanation which is formed in the process of radioactive disintegration. Such compounds of air-dried hydroxides with radium received the name of highly emanating preparations in the science of radioactivity. The methods of their preparation and their properties have been systematically studied by O. Hahn and his co-workers in recent years. Their research resulted in important changes and in the simplification of the technical methods of obtaining emanation. By the use of these preparations it is now possible to obtain emanation, as for instance for medical purposes, in exactly measured quantities. At the same time a nearly quantitative utilization of the produced emanation is realized. The whole technical equipment has been very much simplified and to obtain emanation it is now necessary only to attach the gold emanation needle to the apparatus.

In spite of the practical importance of these compounds the method of their preparation remained purely empirical. The only theory which received general attention was proposed by O. Hahn[1] some five years ago.

The procedure followed in preparing highly emanating compounds consisted according to Hahn in pouring a barium-radium chloride solution containing ferric ions into a large excess of ammonia and ammonium carbonate or sulfate. The purpose of ammonium carbonate or sulfate was to obtain insoluble radium salts which are adsorbed on ferric hydroxide. The investigation of Hahn and Heidenheim led the authors to the following conclusion: "Insoluble salts of radium are quantitatively precipitated from the solution, even if their solubility product has not been exceeded, if the precipitation is carried out in presence of a large excess of ferric hydroxide."[2]

Erbacher and Kädig have given another method of separating the highly emanating substances. They first precipitate ferric hydroxide and add then radium salt solution. The whole is poured into an excess of ammonium carbonate. The authors noticed that in alkaline solutions radium was quanti-

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[1] O. Hahn and Heidenheim: Ber., **59**, 284 (1926).

[2] According to this point of view radium is precipitated as carbonate if ammonium carbonate is present, etc. Ferric hydroxide is considered to be only a carrier of the radium containing substance. See: Hahn and Müller: Z. Elektrochemie, **27**, 189 (1923); Hahn: Ann., **440**, 121 (1924); Hahn: Naturwissenschaften, **12**, 1140 (1924); Hahn, Erbacher, Feichtinger: Ber., **59**, 2014 (1926); Hahn and Z. Biltz: Z. physik. Chem., **126**, 323; Biltz: 356 (1927); Hahn: Ann., **462**, 174 (1928); Hahn: Naturwissenschaften, **15**, 295 (1930).

tatively removed from the solution even before addition of ammonium carbonate. Nevertheless, they think that it is necessary to add some anions forming insoluble radium salts to prevent a subsequent desorption of radium from the ferric hydroxide.

Another theory can be proposed which is consistent with the preparation method, and is based on the colloidal properties of the precipitates. The hydroxides contain, as it is well known, varying quantities of anions (SO_4^{--}) in bound condition, depending on the pH of the solution. We may assume then that the adsorption of radium depends on the presence of these anions. The hydroxide resembles then a labile compound of changing composition corresponding to the pH of the solution in which it is present. According to this view it is natural to expect that radium would be uniformly distributed throughout the precipitate and would not be present in the form of submicroscopic crystals adhering to the hydroxide. This theory has received now a satisfactory experimental confirmation as will be seen from the following:

The Experimental Part

For the following experiments not radium but its isotope thorium X was chosen because a rapid determination of the radio-active content of the solution and of the precipitate by the emanation method is then possible.

It seemed to be desirable to establish first the fact whether the ions SO_4^{--} and HCO_3^- have any influence on the amount of radium precipitated on ferric hydroxide. A series of experiments with this purpose in view has been made and the results will be clear from the following examples.

Two solutions were prepared containing each: Fe^{+++}: 0.0797 gr., Th X ; 2.84×10^{-3} gr.[3] and Cl^- and NO_3^- ions in 500 cc. The second of these solutions contained some SO_4^{--} ions in addition. Ferric hydroxide was precipitated from both solutions by adding ammonia. After a period of four hours samples of solution were withdrawn. No Th X could be detected showing that the whole of it was adsorbed on the precipitate. To the remainder of the solutions hydrochloric acid was added until ferric hydroxide became flocky while remaining still in the precipitate. After another four hours samples of the clear solution were again withdrawn and Th X determined. The following Table I shows the results:

<div align="center">

TABLE I

Effect of SO_4^{--} on the Adsorption of Th X

</div>

Contents before the experiment in one cc. of solution	Th X (Th-units) after the experiment in one cc. of solution	Th X in % of total quantity (2.84×10^{-3} gr.)	
		in solution	in precipitate
1. solution			
5.68×10^{-6} Th X	2.92×10^{-6} gr.	51.4	48.6
2. solution (containing SO_4^{--})			
5.68×10^{-6} Th X	4.80×10^{-6} gr.	84.5	15.5

[3] Th X is given here and in the following in Th units which give grams of thorium in equilibrium with the present quantity of Th X. All experiments in the following were performed using portions of the same standard solution containing Th, Msth1, Rdth and Th X in radioactive equilibrium.

It will be seen that the presence of SO_4^{--} does not increase the amount of Th X precipitated with ferric hydroxide. The following experiment shows whether the presence of SO_4^{--} has any influence on the free exchange of Th X between the precipitate and the solution or not.

A solution containing Fe^{+++} : 0.0793 gr.; Th X : 2.84 × 10⁻⁸ gr. Cl^-, NO_3^- and 0.1 normal SO_4^{--} ions in 500 cc. was made. Strong ammonia was added and 50 cc. of the solution analyzed for Th X. Found 1.2 × 10⁻⁶ gr. Th X per cc. or 21% of the total Th X in solution. The remaining solution was then neutralized with HCl and Th X again determined. Found: 5.15 × 10⁻⁶ gr. Th X per cc. or 92.7% of it in solution. Strong ammonia was added to the rest again and a determination of Th X made. No Th X could be found in solution. It is seen thus that the ion SO_4^{--} does not prevent free exchange of Th X between the precipitate and the solution.

In the same manner it has been established that the HCO_3^- ion does not prevent this exchange either. A solution containing Fe^{+++} 0.0793 gr. Th X 2.84 × 10⁻⁸ gr., Cl^-, NO_3^- in 500 cc. was made. It was boiled and the precipitation carried out with a large excess of ammonia. All reagents were carefully purified from traces of CO_2 and all work was carried out in a closed space free of CO_2. No Th X could be detected in 50 cc. of solution, showing that it was quantitatively precipitated with ferric hydroxide.

A solution identical with the preceding one was now made and precipitation made without adding an excess of ammonia. Found: 4.9 × 10⁻⁶ gr. Th X per cc. or 86.3% of it in solution. Another such solution was precipitated with a small amount of dilute ammonia to which 10% ammonium carbonate was added. Found 4.7 × 10⁻⁶ gr. per cc. or 82.8% Th X in solution. A large excess of ammonia was later added to this solution. No Th X could be detected in solution.

The preceding experiments show clearly that adsorption of Th X—and therefore of Ra—is determined by the alkalinity of the solution above. In the following experiments the dependence of Th X adsorption upon the pH of solutions was quantitatively studied. The experiments were carried out in the following manner. To a solution containing known quantities of ferric ion and Th X some ammonia was added. A sample of the solution was withdrawn and Th X and pH determined. More ammonia was added to the remainder and a sample again withdrawn. In such a manner from 3 to 6 determinations of Th X at varying pH could be made with one solution. The determination of Th X in sample solutions was made as follows. The sample was poured into a special glass vessel, acidulated with HCl and made up to a constant volume. Air was blown through the solution and then through the ionization chamber at constant rate. The ionization was measured with a unifilar electrometer. The apparatus was calibrated before and after each determination by determining the ionization produced by a standard solution of thorium in equilibrium with its disintegration products.

A sample determination:

1. Natural ionization before the experiment: 2.36 scale divisions per minute or 0.036 volts per minute (Electrometer sensitivity 65.0 divisions per volt).

2. Natural ionization after the experiment 2.19 scale divisions per minute or 0.034 volts per minute (Electrometer sensitivity 64.5 scale divisions per volt).

3. Ionization produced by the standard Th solution containing 1.57×10^{-3} gr. Th X (in Th units of course) 0.36 volts per minute (Mean of 0.372 and 0.348).

4. The unknown solution produced ionization equivalent to 0.042 volts per minute. It contains therefore:

$$\frac{1.57 \times 10^{-3} \times 0.042}{0.36} = 1.84 \times 10^{-6} \text{ gr. Th X}$$

The pH of solutions was determined with the aid of quinhydrone calomel electrodes. A potentiometer and a Hartmann and Braun mirror galvanometer were used. In the following Table II are given the results of these experiments.

TABLE II

The Dependence of Th X Adsorption on the pH of Solutions

$t = 17°$ C.

pH	Th X used for the experiment		Th X found in the solution		% Th X in pre-cipitation
	Total	in 1 cc.	in 1 cc.	% of total quantity	
Solution No. 6 contains:		a) Th X—7.80×10^{-3} gr.			
		b) Fe—0.0793 gr.			
5.09	7.8×10^{-3}	3.12^{-5}	2.97^{-5}	100.	——
6.48	5.34×10^{-3}	2.72×10^{-5}	2.40×10^{-5}	88.2	11.8
7.6	4.195×10^{-3}	1.70×10^{-5}	0.74×10^{-5}	33.17	66.83
Solution No. 7 contains:		a) Th X—3.90 $\times 10^{-3}$ gr.			
		b) Fe—0.0793 gr.			
4.24	3.9×10^{-3}	1.56×10^{-5}	1.52×10^{-5}	100.	——
4.37	3.12×10^{-3}	1.56×10^{-5}	1.73×10^{-5}	100.	——
5.00	1.46×10^{-3}	1.39×10^{-5}	1.43×10^{-5}	100.	——
7.20	1.95×10^{-3}	1.39×10^{-5}	0.70×10^{-5}	50.25	49.75
Solution No. 8 contains:		a) Th X—7.8×10^{-3} gr.			
		b) Fe—0.1586 gr.			
5.36	7.8×10^{-3}	3.12×10^{-5}	2.88×10^{-5}	92.5	7.5
7.68	4.51×10^{-3}	2.61×10^{-5}	0.60×10^{-5}	23.1	76.9
7.53	2.43×10^{-3}	1.64×10^{-5}	0.22×10^{-5}	13.15	86.85
8.25	1.98×10^{-3}	1.46×10^{-5}	——	——	100.0
Solution No. 9 contains:		a) Th X—19.5×10^{-3} gr.			
		b) Fe—0.1586 gr.			
4.7	19.5×10^{-3}	3.9×10^{-5}	4.01^{-5}	100.	——
5.99	15.6×10^{-3}	3.81×10^{-5}	3.80×10^{-5}	100.	——
5.99	12.55×10^{-3}	3.69×10^{-5}	3.70×10^{-5}	100.	——
6.23	9.60×10^{-3}	3.62×10^{-5}	3.40×10^{-5}	94.	6.
6.90	6.70×10^{-3}	3.40×10^{-5}	2.04×10^{-5}	60.	40.
7.54	4.68×10^{-3}	2.92×10^{-5}	0.42×10^{-5}	14.4	85.6

The last two columns of the table give the percentage of Th X in solution and in the precipitate. Since, however, the experiments were performed with different amounts of Th X and ferric hydroxide present, the following Table III gives the results recalculated for the case of a solution containing the same quantity of ferric hydroxide, 0.1586 gr.

TABLE III

Th X adsorbed at Different pH

pH	Th X in 1 cc. of solution	Th X in 0.1586 gr. of of ferric hydroxide
5.99	3.80×10^{-5}	——
6.23	3.4×10^{-5}	0.58×10^{-3}
6.48	2.4×10^{-5}	1.26×10^{-3}
6.90	2.04×10^{-5}	2.62×10^{-3}
7.20	0.70×10^{-5}	1.94×10^{-3}
7.54	0.42×10^{-5}	3.49×10^{-3}
7.60	0.74×10^{-5}	5.60×10^{-3}
7.68	0.60×10^{-5}	3.47×10^{-3}
7.53	0.22×10^{-5}	2.11×10^{-3}
8.25	——	3.80×10^{-3}

The precipitated ferric hydroxide contains Rdth from the standard Th X solution. The question arises whether Th X produced by Rdth is freely exchanged with the solution or whether it is retained in the precipitate. In the first case one should expect that, when a solution is maintained at constant pH, the amount of Th X in solution will not change with time, in the second case it should decrease due to its radioactive decay. A solution identical with solution No. 1 described on the previous pages and containing ferric hydroxide on the bottom was kept at pH 6-7 for a longer period of time. It contained at the beginning of the experiment 2.55×10^{-3} gr. Th X. The following results were obtained:

TABLE IV

The Change of Th X in Solution with Time

Time from the beginning of the experiment	Volume of the Solution	Th X in 1 cc. of solution (gr.)	Th X in the whole solution (gr.)	Calculated quantity of Th X (gr.)
45 hours	900 cc.	2.88×10^{-6}	2.59×10^{-3}	2.64×10^{-3}
167 hours	800 cc.	3.39×10^{-6}	2.71×10^{-3}	2.65×10^{-3}
A. 307 hours	700 cc.	1.84×10^{-6}	1.29×10^{-3}	2.67×10^{-3}
B. 307 hours	600 cc.	3.81×10^{-6}	2.28×10^{-3}	2.49×10^{-3}

Before taking the first and second samples of this experiment the solution was shaken. For the third sample it was not shaken while for the fourth it was warmed up and shaken. The calculation of Th X in solution (last column)

was made assuming a free exchange between precipitate and solution. A typical calculation is given below for the 45 hour sample:

1. The quantity of Th X remaining in the solution considering the decay: 1.79×10^{-3} gr.

2. Th X produced by 2.84×10^{-3} gr. Rdth (45 hrs.) 0.85×10^{-3} gr.

3. The total Th X in solution: 2.64×10^{-3} gr.

The agreement of calculated and determined quantities shows that the concentration of Th X in solution is maintained by Th X rising from Rdth in the precipitate. Four solutions were now made containing equal quantities of ferric ion and Th X. They were precipitated with different amounts of ammonia. After thirteen and fifteen days two samples were taken from each solution (after shaking) and Th X and pH determined. The following Table V shows the results:

TABLE V

The Amount of Th X in Solution as a Function of Time and pH

No. of the solution	Th X (Th-units) used for the experiment	pH of the solution	Quantity of Th X (Th-units) found in the solution	Remarks
1	1.92×10^{-3} gr.	7.6	not found	pH and Th X
2	1.92×10^{-3} gr.	7.62	not found	measured after 13 days
3	1.92×10^{-3} gr.	5.42	1.71×10^{-3} gr.	pH and Th X
4	1.92×10^{-3} gr.	4.6	1.82×10^{-3} gr.	measured after 15 days

It will be seen that Th X is freely exchanged between the precipitate and the solution when the solution has a pH between 5 and 6 but that the exchange is absent when pH exceeds 7. These experiments were performed in absence of SO_4^{--} and HCO_3^{-} ions.

Discussion of the Results

The experiments described on the previous pages show quite conclusively that the opinion, that ferric hydroxide (and similarly other hyrdoxides) is simply a carrier of a distinct radioactive compound, is untenable. Instead it must be assumed that the precipitation of radium together with ferric hydroxide in alkaline media depends on the formation of a salt-like compound in which radium acts as a cation and ferric hydroxide as anion. This is established by the observations that the presence of neither SO_4^{--} nor HCO_3^{-} ions is necessary to produce highly emanating preparates. Thus the procedure of obtaining these is simplified still further. A more detailed study shows, that at pH higher than 7, Th X is firmly adsorbed by the hydroxide. At pH lower than 7 Th X originally adsorbed or produced by Rdth is freely exchanged with the solution. The exact point on the pH scale at which Th X (or radium) is adsorbed on ferric hydroxide or is desorbed from it can not be given, of course.

The experiments here described show also that in order to obtain the highly emanating preparates the solubility product of pure radium salt (or of the isomorphous Ba-Ra salts) should not be exceeded in the solution. This is contrary to the earlier views on the subject but is in accord with the observations of Erbacher and Kädig (loc. cit.) who found that by precipitating Ra and Ba salts with large amounts of ammonium chromate preparates of diminished emanating activity were obtained. By exceeding the solubility product of Ra salts they obtained these in the form of microscopic crystals instead of having Ra uniformly distributed throughout the mass of the hydroxide, a state which obtains when Ra is fixed on the ferric hydroxide in presence of ammonium chromate.

This work has been carried out in the Chemical Laboratory of the University of Moskau.

Summary

1. The properties and the methods of preparation of the highly emanating Ra preparates are described.

2. It is shown that the fixation of Th X (and Ra) on ferric hydroxide does not depend on the presence of some anions forming insoluble Ra salts but is entirely determined by the pH of the solution.

3. The structure of the highly emanating preparates is described.

TRANSMISSION SPECTRA OF DYES IN THE SOLID STATE[*]

BY W. C. HOLMES[1] AND A. R. PETERSON[2]

Practically no data are available in the literature on the transmission of light by dyes in the solid state. The method herein employed consisted in depositing a thin film of "air dried" dye upon a glass slide and interposing it at right angles to the path of one of the parallel beams of light of a visual spectrophotometer.

The dye films were obtained by the evaporation of aqueous or alcoholic solutions of the dyes. With many dyes it is difficult or impossible to obtain continuous films in this manner without resorting to the employment of gelatine or similar agents which it was desired to exclude. It was found possible to obtain deposits of a reasonably satisfactory character, however, with numerous azo, triphenylmethane, and xanthene dyes. In such instances the only difficulty involved was that of regulating the thickness of the dye film within limits wherein its light absorption could be measured advantageously.

Typical absorption measurements obtained with such films are recorded in Table I. The dyes investigated were representative samples of commercial grade which were, in nearly all instances, recrystallized before use. The numbers recorded with them are their list numbers in the Colour Index of the Society of Dyers and Colourists (Bradford, England, 1924). Aqueous solutions were employed in obtaining these films of azo dyes and alcoholic solutions in obtaining those of dyes of other classes. The tabulated values are Bunsen extinction coefficients.

Discussion

Although the spectra of solid dyes frequently differ considerably from the spectra of their dilute solutions, they exhibit no features which are exclusively characteristic of the solid state. The outstanding modifications in spectra which occur when dyes are dissolved are (1) a shifting in the spectral location of the absorption band, attended by (2) evidences of increasing molecular dispersion and, frequently, by (3) evidences of tautomeric alteration in the dye. The first of these phenomena, however, also occurs in passing from one solvent to another, and evidences of increasing dispersion and of tautomerism which are of the same type, if not of equal degree, are often observed upon the mere dilution of aqueous dye solutions.[3]

TABLE I

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

Part 1—Azo Dyes

Colour Index No.	Janus Green B 133	Dianil Blue R 309	Niagara Blue 3RD 468	Pontamine Blue AX 502	Niagara Blue RW 512	Pontamine Sky Blue 6BX 518	Pontamine Sky Blue 5BX 520
				E			
460 mμ	—	—	—	—	—	—	—
480 "	—	—	—	—	—	—	—
490 "	—	—	—	—	—	—	—
500 "	0.42	0.57	1.38	0.70	0.56	0.56	0.65
510 "	0.42	0.62	1.42	0.74	0.62	0.66	0.73
520 "	0.43	0.66	1.45	0.78	0.69	0.77	0.82
530 "	0.48	0.69	1.48	0.83	0.76	0.90	0.92
540 "	0.55	0.72	1.50	0.86	0.84	1.03	1.02
550 "	0.63	0.75	1.50	0.89	0.94	1.15	1.09
560 "	0.69	0.77	1.49	0.92	1.03	1.27	1.16
570 "	0.72	0.78	1.48	0.94	1.09	1.36	1.23
580 "	0.75	0.77	1.46	0.95	1.16	1.45	1.28
590 "	0.78	0.765	1.43	0.96	1.21	1.50	1.32
600 "	0.81	0.76	1.40	0.95	1.27	1.50	1.36
610 "	0.83	0.74	1.36	0.92	1.32	1.44	1.40
620 "	0.84	0.72	1.32	0.90	1.35	1.35	1.42
630 "	0.82	0.69	1.25	0.87	1.33	1.23	1.39
640 "	0.79	0.67	1.18	0.85	1.25	1.17	1.35
650 "	0.74	0.64	1.10	0.87	1.21	1.11	1.32
660 "	0.68	0.62	1.03	0.87	1.19	1.05	1.30
670 "	0.63	0.59	0.95	0.80	1.22	0.95	1.29
680 "	0.58	0.56	0.88	0.73	1.24	0.83	1.30
690 "	0.52	0.54	0.84	0.67	1.16	0.70	1.30
700 "	0.45	0.51	0.81	0.62	0.97	0.57	1.27

Part 2—Triphenylmethane Dyes

Colour Index No.	Victoria Green 657	Brilliant Green 662	Alphazurine FG 671	Xylene Blue VS 672	Pararosaniline 676	Crystal Violet 681	Ethyl Violet 682	Acid Fuchsine 692
				E				
460 mμ	—	—	—	—	—	—	—	0.80
480 "	—	—	—	—	0.72	—	—	1.10
490 "	—	—	—	—	0.77	—	—	1.18
500 "	0.12	0.07	0.28	0.15	0.82	0.77	0.62	1.23
510 "	0.16	0.10	0.30	0.22	0.87	0.91	0.80	1.23
520 "	0.25	0.14	0.36	0.30	0.89	1.07	0.95	1.20
530 "	0.40	0.21	0.44	0.46	0.89	1.18	1.08	1.17
540 "	0.60	0.35	0.54	0.68	0.88	1.22	1.19	1.15
550 "	0.80	0.52	0.73	0.89	0.87	1.19	1.27	1.10
560 "	0.99	0.71	0.98	1.28	0.85	1.13	1.30	1.04

TABLE I (continued)

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

Colour Index No.	Victoria Green 657	Brilliant Green 662	Alphazurine FG 671	Xylene Blue VS 672	Pararosaniline 676	Crystal Violet 681	Ethyl Violet 682	Acid Fuchsine 692
				E				
570 "	1.13	0.86	1.29	1.53	0.83	1.06	1.30	0.96
580 "	1.23	0.98	1.60	1.77	0.81	0.97	1.27	0.84
590 "	1.29	1.06	1.77	1.95	0.75	0.90	1.19	0.70
600 "	1.31	1.11	1.89	2.07	0.67	0.83	1.15	0.58
610 "	1.29	1.09	1.93	2.10	0.61	0.78	1.12	0.46
620 "	1.24	1.06	1.96	2.12	0.54	0.73	1.08	0.35
630 "	1.22	1.06	2.02	2.12	0.46	0.68	1.00	—
640 "	1.22	1.07	2.03	2.19	0.40	0.63	0.88	—
650 "	1.20	1.03	2.02	2.29	0.35	0.56	0.72	—
660 "	1.16	0.96	1.95	2.36	0.32	0.48	0.56	—
670 "	1.05	0.86	1.80	2.32	0.30	0.38	0.41	—
680 "	0.90	0.75	1.29	2.26	0.29	0.28	0.27	—
690 "	0.65	0.61	0.69	2.07	—	0.21	—	—
700 "	0.41	0.58	0.37	1.90	—	0.16	—	—

Part 3—Xanthene Dyes

Colour Index No.	Pontamine Violet C4B 698	Victoria Blue B 729	Pyronine G 739	Pyronine B 741	Rhodamine B 749	Rhodamine G 750	Rhodamine 3B 751	Violamine B 757
				E				
460 mμ	—	—	—	—	—	—	0.33	—
480 "	—	—	0.95	—	—	—	0.45	—
490 "	—	—	1.01	—	—	—	0.60	—
500 "	0.25	0.23	1.04	1.48	0.35	0.56	0.71	0.37
510 "	0.34	0.36	1.05	1.59	0.44	0.69	0.79	0.48
520 "	0.48	0.50	1.04	1.66	0.53	0.86	0.82	0.67
530 "	0.67	0.66	1.02	1.70	0.61	0.95	0.83	0.83
540 "	0.81	0.83	0.95	1.58	0.62	0.95	0.85	0.95
550 "	0.89	0.96	0.89	1.45	0.62	1.00	0.87	1.02
560 "	0.88	1.06	0.84	1.40	0.66	1.07	0.87	1.05
570 "	0.81	1.12	0.80	1.30	0.68	1.12	0.83	1.00
580 "	0.75	1.15	0.76	1.13	0.67	1.06	0.76	0.93
590 "	0.68	1.15	0.70	0.86	0.60	0.84	0.60	0.82
600 "	0.64	1.13	0.63	0.59	0.36	0.52	0.42	0.66
610 "	0.60	1.10	0.57	0.33	0.18	0.23	0.31	0.54
620 "	0.55	1.09	0.50	0.19	0.11	—	0.25	0.40
630 "	0.47	1.06	0.45	0.11	—	—	—	0.27
640 "	0.36	1.01	0.40	—	—	—	—	0.19
650 "	0.27	0.96	—	—	—	—	—	0.12

TABLE I (continued)

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

Colour Index No.	Pontamine Violet C4B 698	Victoria Blue B 729	Pyronine G 739	Pyronine B 741	Rhodamine B 749	Rhodamine G 750	Rhodamine 3B 751	Violamine B 757
				E				
660 "	0.18	0.91	—	—	—	—	—	0.07
670 "	0.13	0.83	—	—	—	—	—	—
680 "	0.10	0.73	—	—	—	—	—	—
690 "	—	0.62	—	—	—·	—	—	—
700 "	—	0.51	—	—	—	—	—	—

Part 4—Xanthene Dyes

Colour Index No.	Violamine RR 758	Violamine G 759	Uranine 766	Eosine 768	Ethyl Eosine 770	Eosine B 771	Erythrosine 773	Phloxine B 778	Rose Bengal B 779
					E				
460 mμ	—	—	0.82	0.30	0.44	0.43	0.21	0.68	—
480 "	—	0.27	1.10	0.60	0.70	0.58	0.52	0.88	0.43
490 "	0.60	0.40	1.05	0.83	0.97	0.72	0.71	0.93	0.67
500 "	0.78	0.53	1.10	0.95	1.19	0.90	0.92	0.97	0.90
510 "	1.02	0.67	1.06	0.89	1.20	1.00	1.06	1.00	1.10
520 "	1.23	0.81	0.83	0.86	1.10	1.05	1.02	1.00	1.09
530 "	1.33	0.92	0.52	0.85	1.13	1.06	0.99	0.97	1.03
540 "	1.42	0.95	0.27	0.72	1.17	1.04	0.91	1.04	1.15
550 "	1.40	0.89	0.14	0.53	1.11	0.95	0.75	1.13	1.27
560 "	1.30	0.78	—	0.32	0.92	0.82	0.53	1.23	1.13
570 "	1.15	0.60	—	0.17	0.67	0.68	0.33	1.35	0.80
580 "	0.92	0.38	—	0.10	0.38	0.52	0.19	1.28	0.45
590 "	0.69	0.21	—	—	0.23	0.38	0.11	0.75	0.18
600 "	0.47	—	—	—	0.16	0.26	—	0.38	0.08
610 "	0.31	—	—	—	—	0.17	—	0.23	—
620 "	0.19	—	—	—	—	0.11	—	—	—
630 "	—	—·	—	—	—	—	—	—	—
640 "	—	—	—	—	—	—	—	—	—
650 "	—	—	—	—	—	—	—	—	—
660 "	—	—	—	—	—	—	—	—	—
670 "	—	—	—	—	—	—	—	—	—
680 "	—	—	—	—	—	—	—	—	—
690 "	—	—	—	—	—	—	—	—	—
700 "	—	—	—	—	—	—	—	—	—

Fig. 1 affords a comparison of the absorption spectrum in the solid state with spectra of dilute alcoholic and aqueous solutions of several of the dyes investigated.
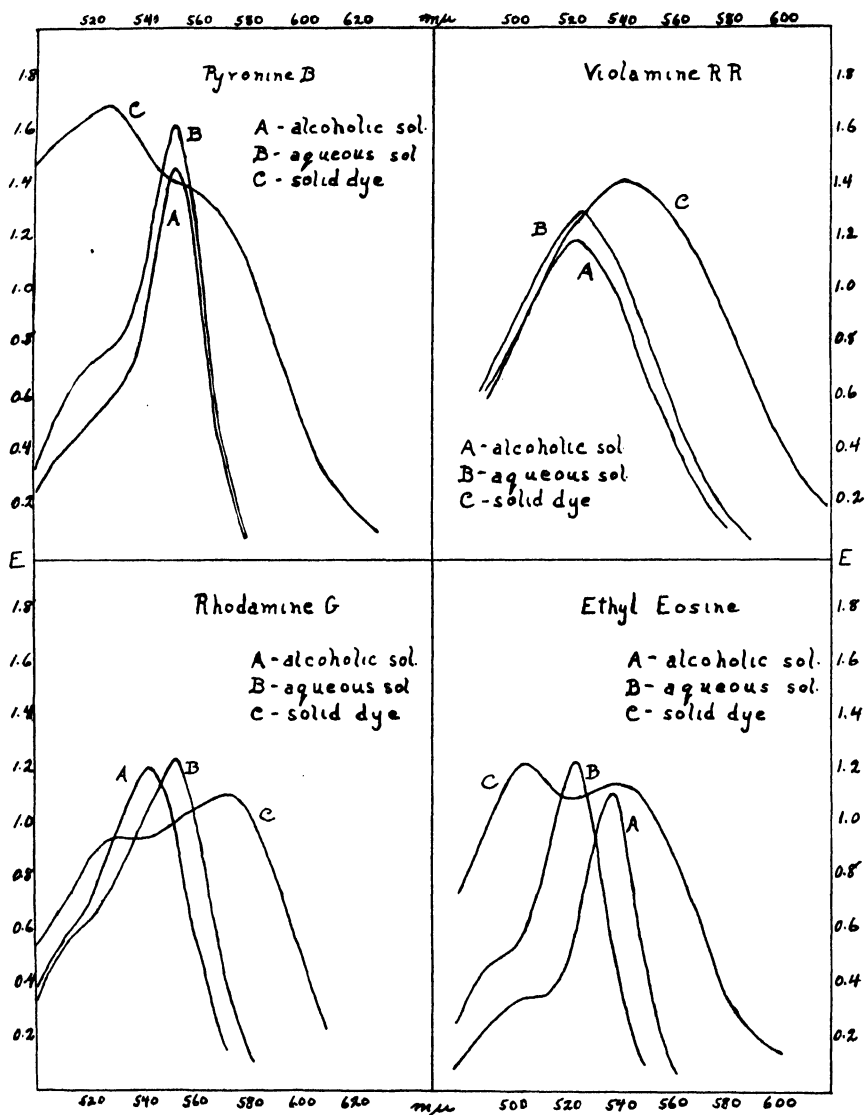
FIG. 1

A comparison of the spectra of solid dyes with the spectra of their aqueous and alcoholic solutions indicates that the effect of solution upon the hue of the dye is intrinsically hypsochromic. The practical effect, however, may frequently be the reverse. This anomaly arises from the fact that the hue of many dyes is a composite hue of two isomeric forms, and that the solution

of such dyes is attended by an alteration in the equilibrium between the tautomers which exerts an effect upon the composite hue which is opposite in type and greater in degree than is the direct effect of solution. Thus, Crystal Violet exists in two tautomeric forms with decidedly different hues, of which the lighter predominates in the solid state. The hue of each dye form becomes lighter when the dye is dissolved, but solution is attended by such extensive conversion of the lighter dye form into the deeper that the hues of solutions are decidedly deeper than that of the dye. The general effect of solution, however, is to displace absorption bands in the direction of shorter wave length, and dye solutions are lighter in hue than are the dyes from which they are prepared when tautomerism does not exert a preponderant effect.

In general, the absorption bands of solid dyes are decidedly broader in proportion to their height than are those of their solutions. The depression of band maxima and the broadening of their slopes are criteria of increasing molecular aggregation[4] and would be anticipated in passing from solution to the solid state. In the instance of Brilliant Green, the phenomenon of increasing molecular aggregation was observable in the solid state. Freshly prepared dry films of dye absorbed light in the manner indicated by the tabulated measurements, but the absorption bands became distinctly broader and less well defined within a few hours.

Previous investigation of aqueous solutions of dyes has demonstrated that many dyes undergo tautomeric alterations of one type or another. The data of Table I are of interest because of the further evidence which they afford for that conclusion.

Numerous indications of tautomerism in aqueous solutions of azo dyes of diverse character have been noted,[3] and Brode[5] has recently established the tautomeric nature of even a very simple type of azo dye. The measurements with solid azo dyes indicate a type of tautomerism in disazo dyes prepared from dianisidine which appears characteristic for that dye type.

The type of tautomerism illustrated in the instance of Ethyl Eosine (Fig. 1) has been observed previously in fluoresceine and in its halogenated derivatives substituted within the phthalic anhydride residue.[3] The examination of solid dyes has now shown that it also occurs in the more important dyes of the same group in which substitution occurs within the resorcin residues. Similar results to those reported have also been obtained with several kindred dyes of laboratory preparation, and it may now be stated that all the dyes of the group which are substituted exclusively by halogens exist in two tautomeric forms. This tautomerism may be suppressed, however, by other types of substitution. Neither Eosine B (Table I) nor mercurochrome give evidence of tautomerism.

It appears very probable that tautomerism in this dye group must originate in changes in the character of the quinoid oxygen bonding. The most obvious explanation which might be suggested is that of tautomerism between an anhydrous dye form in which the oxygen is typically quinoid and a hydrated

[4] Pihlblad: Z. physik. Chem., 81, 417 (1912).

[5] Brode: J. Am. Chem. Soc., 51, 1204 (1929).

dye form in which it is replaced by two hydroxyl groups in the hemiquinoid arrangement. Although the typically quinoid structure has been assigned to the dyes of this group for many years, it has recently been shown that they retain the elements of a molecule of water with great tenacity and that their structure is probably hemiquinoid.[6,7] It is by no means clear, however, that actual tautomerism occurs between quinoid and hemiquinoid structure.

The previous study of dye solutions has demonstrated that aminated dyes of the triphenylmethane, xanthene and quinonimide classes undergo a striking tautomeric alteration with the dilution of their aqueous solutions.[3] This phenomenon has been observed with a very large number of such dyes, including many of those which are of great importance in scientific applications. In general a decided degree of tautomeric alteration could be noted with any considerable variation in the dye concentration of aqueous solutions. With basic and acid fuchsines and with diamino derivatives in the triphenylmethane dye group, however, the degree of tautomeric alteration observable was very small, and the violamines in the xanthene dye group appeared stable.

The recorded series of measurements on solid dyes indicate very clearly that basic and acid fuchsines, and that diamino derivatives of the triphenylmethane series in general, undergo decided degrees of tautomeric modifications, differing from other triphenylmethane dyes only in respect to the variation in conditions which is required to render them manifest. On the other hand, the measurements on violamines in the solid state give no indication whatever of the presence of more than one dye form.

It now appears, accordingly, that the violamines probably constitute the sole exception to the general rule that aminated triphenylmethane, xanthene and quinonimide dyes exist in two tautomeric forms. This fact seems significant. A hypothesis has been advanced which refers this type of tautomerism to valence rearrangements, occurring within the salt-forming amino group, which involve a tautomerism between trivalent and pentavalent bonding of the nitrogen atom.[8] The violamines are unique among the dye classes referred to in respect to the fact that they do not allow a pentavalent amino arrangement. They are structurally incapable, accordingly, of the type of tautomerism postulated and would be expected to prove stable on the basis of the hypothesis in question.

Summary

(1) Transmission spectra are recorded of thirty-two azo, triphenylmethane and xanthene dyes in the solid state.

(2) Solution is found to displace the absorption bands in the direction of shorter wave length.

(3) The data indicate a high degree of molecular aggregation in dry dyes.

(4) New evidence is afforded on the occurrence and degree of tautomerism in dyes.

[6] Gomberg and Tabern: J. Ind. Eng. Chem., **14**, 1115 (1922).

[7] Holmes and Scanlan: J. Am. Chem. Soc., **49**, 1594 (1927).

[8] Holmes: Stain Tech., **1**, 116 (1926).

THE SURFACE CHEMISTRY OF HYDRATES. II
Decomposition without Lattice Rearrangement*

BY V. R. DAMERELL, F. HOVORKA AND W. E. WHITE

Introduction

According to classical theory, a hydrate or related substance will decompose below a certain vapor pressure or above a certain temperature, yielding a lower hydrate or anhydrous substance and water vapor. During this transition, the vapor pressure of the system will remain constant at a given temperature as long as any of the higher hydrate remains, since in phase rule terminology the system is univariant; also, the lattice structure will rearrange as the dehydration progresses, forming that of the lower hydrate or anhydrous substance. It is to be noted that most hydrates which behave experimentally in accordance with this theory have been studied at temperatures not very far below their transition temperatures.

In a recent article,[1] however, a finely divided trihydrate of alumina was described which appeared to break up at room temperature differently than in the manner described above. The composition of this hydrate was obtained by the approximation equation

$$\frac{w_1 - c}{w_s - c} = \frac{w'_1 - c}{w'_s - c} \tag{1}$$

where w_1 and w_s represent the total number of molecules of water per molecule of alumina (adsorbed and chemically combined) contained by two samples of the substance over the same water vapor pressure source, the two samples having a different average particle size; w'_1 and w'_s represent the total number of molecules of water per molecule of alumina for the same two samples over a different water vapor pressure source; and c is the number of molecules of water of crystallization per molecule of alumina. Since the various values for w can be obtained experimentally, c is given by

$$c = \frac{w_1 w'_s - w_s w'_1}{w_1 + w'_s - w_s - w'_1} \tag{2}$$

Calculations involving five precipitates of different average particle size showed c to be close to three.

The behaviour of this substance over phosphorus pentoxide indicated the possibility of water being lost from the surface without appreciable rearrangement of the remaining lattice structure. The work presented herein was undertaken, therefore, as an investigation of this type of decomposition and its relation to the constant vapor pressure decomposition of hydrates.

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[1] Cf. Damerell: J. Phys. Chem., **35**, 1061 (1931).

Experimental

Preparation of alumina trihydrate.

This substance was prepared by precipitation of hydrous alumina from a solution of aluminum sulfate with ammonium hydroxide, followed by repeated washing at room temperature in the presence of small amounts of ammonia. The details of the preparation are given in an earlier publication,[2] and will not be repeated here. After about two months aging, the precipitate was separated into two portions of a different average size of particle by suspending in water and decanting after a partial settling, as described before. Two precipitates were obtained in this way, and will be designated hereafter as large particle and small particle precipitates. These were filtered off and dried for several days in the air.

This method of separation will be successful only when the disperse phase is composed of primary particles which vary in size, and it is conceivable, as Weiser[3] has pointed out, that the most rapidly settling portion may have been composed of aggregates of primary particles of about the same size having a specific surface that approached the sum of the specific surfaces of the slower settling primary particles. But an earlier experiment of Tartar and Damerell[4] indicates that there is a decided difference in the primary particle size. Aged hydrous alumina was prepared as described above from aluminum nitrate, and after being washed essentially free from nitrate and ammonia was centrifuged out once. The precipitate was shaken with distilled water, with which it formed a stable colloidal suspension of the settling type. Portions were taken from the top, middle and bottom of this suspension after it had been allowed to settle partially, and each was analyzed for alumina in the usual manner. From the analyses, a sol was made up from each containing just 0.85 grams of alumina per liter. A sufficient amount of basic aluminum chloride solution was now added to each portion so that the chlorine concentration became 0.355 grams per liter. Such mixtures always increased in acidity upon standing, probably due to a preferential ion adsorption. The hydrogen ion activities in the experiment in question after equilibrium was reached were as follows.

Grams of chlorine per liter from basic aluminum chloride	Portion of colloidal suspension taken	pH
0.355	top	3.825
0.355	middle	3.87
0.355	bottom	3.94
0.355	(distilled water)	4.03

This is considered as evidence for a different primary particle size.

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[2] See reference 1, page 1063.

[3] Private communication.

[4] J. Phys. Chem., **36**, May (1932).

Desiccation experiments.

It was decided to calculate values for c from equation (2) using only w values of less than three, and also to see if the composition of the trihydrate would reach a constant value after long exposure to phosphorus pentoxide. To accomplish this, two samples of the trihydrate, one from the large particle precipitate and the other from the small particle precipitate were put in weighing bottles and kept in a desiccator over phosphorus pentoxide for nearly six months. Each weighing bottle contained about a gram of the sample, sufficiently air-dried beforehand so that it did not adhere to the glass. The desiccator was kept in a constant temperature room having an observed temperature over the six months period of $24° \pm 1°C$. Numerous weighings were made, the procedure being to open the desiccators and immediately put the ground glass covers on the weighing bottles, which were then weighed as rapidly as possible. Care was taken to follow just the same procedure each time as regards order and method of weighing. As the results in Table I show, opening the desiccator every three days seriously slowed up the desiccation, so after constant weight was practically reached using this time interval, the desiccator was opened less and less frequently, being allowed to stand for two months before the final weighing. It is seen from Table I that constant composition was essentially reached when weighing was stopped. The samples were finally ignited for many hours in platinum crucibles, not only until constant weight was reached, but also until the alumina gained practically no weight when allowed to stand on the balance pan after weighing.

TABLE I

Change in composition of the hydrate with time over phosphorus pentoxide

Days between weighing	Composition of the large particle precipitate	Composition of the small particle precipitate
0	$Al_2O_3 . 3.534 \ H_2O$	$Al_2O_3 . 3.207 \ H_2O$
2	2.996	2.965
2	2.975	2.944
3	2.966	2.933
3	2.960	2.926
3	2.958	2.925
3	2.958	2.924
3	2.957	2.924
3	2.955	2.923
3	2.956	2.922
3	2.956	2.921
3	2.955	2.921
3	2.954	2.921
7	2.946	2.907
15	2.939	2.900
27	2.934	2.893
35	2.930	2.888
62	2.928	2.888

From the resulting water contents given in Table I, it is possible to calculate a great many values for c. Since the large particle and small particle samples must be in a comparable condition before the calculation can have any meaning, the first two values given in the table cannot be used, as the large particle precipitate was obviously in a more moist condition than the small particle precipitate at the start. It is seen by comparing the water lost each time that the two samples were in a similar state about the fourth day. In Table II are given several values for c, together with the values of w used in the calculations.
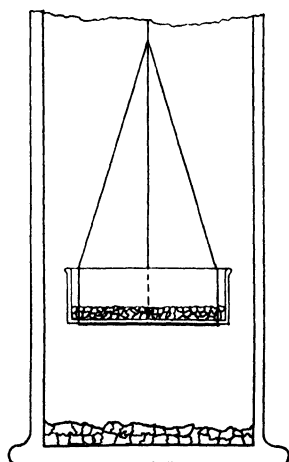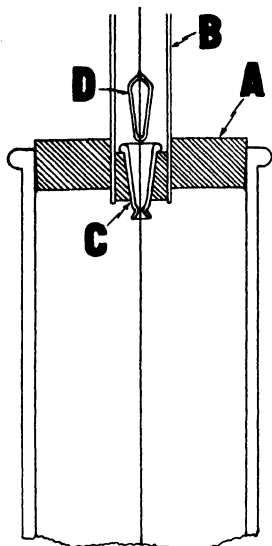
TABLE II

Calculations for c from equation (2)

w_s	w_1	w'_s	w'_1	c
2.923	2.955	2.888	2.928	3.1
2.926	2.960	2.888	2.928	3.2
2.922	2.956	2.893	2.934	3.1
2.933	2.966	2.893	2.934	3.1
2.944	2.975	2.888	2.928	3.1

Determination of the change in water content with vapor pressure.

It was decided to determine experimentally the composition-vapor pressure curve at 25°, and for this purpose a special apparatus, shown in Fig. 1, was built. A glass cylinder was fitted with a stopper (A) and glass tube (B), and another stopper containing the exterior part of a conical ground glass joint (C) was inserted in this tube as shown. The inner part of this joint (D) was pulled out at each end and fused around a platinum wire. The lower end of the platinum wire held a glass container in which was placed about ten grams of the small particle trihydrate precipitate. A hole was drilled in the floor of a balance just under the left hand pan support, and the upper end of the platinum wire went through this hole and ended in a loop by which it could be attached to the pan support. The drawing shows the wire and ground glass stopper as they were during weighings. At all other times the stopper was lowered into place, closing the apparatus. The glass cylinder was immersed in a thermostat, kept at 25° ± 0.1°C, and the desired hydrate or desiccant was placed in the bottom. When the time came to change the water vapor pressure

Fig. 1

TABLE III

Composition of alumina trihydrate over various hydrates at 25°C

Hours between weighing	Hydrate	Millimeters Vapor pressure	Composition
0	$H_2C_2O_4 \cdot 1.75\ H_2O$	2.69	$Al_2O_3 \cdot 2.973\ H_2O$
12	"	"	2.981
24	"	"	2.993
24	"	"	2.995
30	"	"	2.995
44	$NaOOCCH_3 \cdot 2.3\ H_2O$	6.40	3.058
24	"	"	3.066
29	"	"	3.067
21	"	"	3.068
26	"	"	3.068
120	$CuSO_4 \cdot 4.4\ H_2O$	7.80	3.066
24	"	"	3.066
24	"	"	3.066
96	$MgSO_4 \cdot 6.75\ H_2O$	12.7	3.111
214	"	"	3.151
72	"	"	3.153
24	"	"	3.154
24	"	"	3.154
96	$Na_2HPO_4 \cdot 4.0\ H_2O$	14.51	3.197
19	"	"	3.201
28	"	"	3.202
24	"	"	3.202
20	"	"	3.202
48	$Na_2CO_3 \cdot 9.3\ H_2O$	18.01	3.257
95	"	"	3.276
119	"	"	3.328*
52	"	"	3.295
20	"	"	3.296
23	H_2O	23.52	3.312
144	"	"	3.751
288	"	"	4.079
390	"	"	4.320
88	"	"	4.417
	Final approximated value		5

* Thermostat overheated.

source, stopper (A) was loosened, the cylinder withdrawn, and another one substituted containing the new hydrate.

The trihydrate sample was first dried over phosphorus pentoxide for a few days, and was then allowed to stand over the hydrates listed in Table III in the order given. The vapor pressures of all these hydrates have been accurately determined. Many weighings were made over each hydrate, but to save space only enough of these are given to show the change of composition with time and the final composition over each hydrate. In obtaining the maximum water content the trihydrate was allowed to stand over water for six weeks, with frequent weighings. At the end of this time it was still gaining steadily, so an approximate composition of $Al_2O_3.5H_2O$ was used for this vapor pressure, since for the purpose of this work the upper portion of the vapor pressure curve did not need to be accurately known. The composition-vapor pressure curve is given in Fig. 2. The lower value, over phosphorus pentoxide, was taken from Table I. The vapor pressures of the various hydrates were those obtained by Wilson,[5] Carpenter and Jette,[6] and Baxter and Cooper.[7]

Change of composition with temperature.

The change of composition with increasing temperature was measured using an apparatus quite similar to that shown in Fig. 1. The thermostat was replaced by a thermo-regulated electric oven, and two glass tubes corresponding to (B) of Fig. 1 were used, being put through the top of the oven. A desiccator and metal cover were used in place of the glass cylinder and stopper (A) of Fig. 1. A thermometer and an air-inlet tube also went through this metal cover and through the top of the oven. The stoppers and ground glass joints corresponding to (D) of Fig. 1 were put at the top of the glass tubes, about 20 centimeters from the top of the oven, to avoid possible injury due to heat. The desiccator cover was not air tight, since there were small openings between the cover and the desiccator top, and around the various tubes. It was purposely left this way to provide outlets for the air-stream that was being passed in. This air-stream was dried at room temperature by passing it through two cylinders containing concentrated sulfuric acid and then a third containing barium oxide, which served as a powerful desiccant[8] and removed sulfuric acid spray. About a gram of the trihydrate compound was taken for each experiment, the sample container being smaller than the one shown in Fig. 1. Six of these samples were heated from 119° up to at least 250°, the change in composition of the one given in Table IV being typical. Weighings were made at intervals of 24 hours or longer. Enough of these are given in Table IV to show the change of composition with time at each temperature. In Fig. 3 are shown the curves obtained by plotting compositions at two different time intervals against temperature, using some of the results in Table IV. The upper curve represents the composition after 96 hours at the temperatures

[5] J. Am. Chem. Soc., **43**, 704 (1921).
[6] J. Am. Chem. Soc., **45**, 578 (1923).
[7] J. Am. Chem. Soc., **46**, 923 (1924).
[8] Cf. Booth and McIntyre: Ind. Eng. Chem., Anal. Ed., **2**, 12 (1930).

given. The lower curve shows the composition after 96 additional hours at the same temperatures. The composition at 119° after the second period of 96 hours was obtained by extrapolation from the data given in Table IV.

TABLE IV

Change of composition of the large particle trihydrate precipitate with increasing temperatures

Hours between weighing	Composition of large particle precipitate	Temperature in degrees Centigrade
72	Al_2O_3 . 2.759 H_2O	119° ± 1°
24	2.756	"
24	2.757	"
24	2.678	164° ± 1.5°
72	2.650 .	"
96	2.629	"
48	2.627	"
24	2.626	"
72	2.545	184° ± 2°
24	2.530	"
75	2.481	"
21	2.463	"
72	2.377	"
167	2.201	"
167	2.030	"
143	1.852	"
52	0.419	270° ± 4°
22	0.415	"

X-ray data.

The substance indicated by its adsorption behaviour that it was probably composed of small crystals, since equation (2) would not be expected to hold for amorphous substances. To verify this, the X-ray diffraction pattern was obtained by the powder method. A water cooled Coolidge tube with a molybdenum target was used. The average wave length of the radiation was 0.710 Å. The glass tube containing the sample was a millimeter in diameter, and the distance from the center of this tube to the film was 20.04 centimeters. With a sample of the small particle precipitate, the lines shown in Fig. 4 were obtained, after a 48 hour exposure, using a current of 20 milliamperes and a potential of 32,000 volts.

Discussion of Results

The lines obtained in the diffraction pattern of the trihydrate were sharp, indicating a well defined crystalline structure. This pattern is similar to, but not identical with some of those given by Biltz and Lehrer.[9]

[9] Z. anorg. Chem., **172**, 305 (1928).

The results of the desiccation at room temperature can not be explained readily by assuming the ordinary type of hydrate decomposition, since equation (2) would not be expected to hold if a lower hydrate or anhydrous substance and water had been formed. Furthermore, the composition-time curve does not show the induction period that usually appears at the start when crystalline hydrates that have not been previously desiccated are allowed to decompose in the ordinary manner,[10] although Topley and Hume[11] have pointed out that this need not necessarily be present for very finely divided hydrates.

The evidence given here indicates a surface dehydration at room temperature in which the remaining lattice structure does not appreciably rearrange to form a new solid phase, but remains as a skin on the surface of the crystals, causing a slower and slower loss of water. Such a decomposition would cause the water content to approach a value of less than that required for perfect crystals, and the results in Table I indicate that this is the case. A practically constant composition of $Al_2O_3.2.888 H_2O$ and $Al_2O_3.2.928H_2O$ was reached when samples of the small particle and large particle trihydrate precipitates were desiccated for six months over phosphorus pentoxide. In a decomposition of this type, when dehydration does not penetrate too deeply into the crystal, it should be possible to calculate values of c from equation (2), using values of w of less than three. As seen in Table II, values of c calculated in this way are in good agreement with those obtained earlier[1] using values of w greater than three.

This dehydrated lattice would be expected to undergo some change other than an actual rearrangement, due to the condition of strain produced. In view of the reversible manner in which water is taken up by these hydrates having a high transition temperature[12] after desiccation or even moderate heating, it is probable that this change is not great.

This type of decomposition would cause the system to be bivariant, since from the phase rule standpoint it is behaving like a solid solution. Thus the vapor pressure would be expected to vary with the composition at constant temperature, and from the curve shown in Fig. 2, this appears to be the case. If it be assumed that a monomolecular layer of water molecules in contact with each other is present on trihydrate crystals at a vapor pressure of about 7.5 millimeters, where the curve is most nearly flat, it is possible to calculate the surface per gram molecular weight of the trihydrate. Assuming that each water molecule occupies 9 $Å^2$ of the surface, this works out to be approximately 3.8×10^7 square centimeters. A precipitate composed of cubes of the order of 1×10^{-5} centimeters on the side would have a surface of this size.

The temperature-composition curve given in Fig. 3 shows roughly the relationship between surface dehydration without lattice rearrangement and the ordinary type of hydrate decomposition. It was found that when air

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[10] Cf. Rae: J. Chem. Soc., 109, 1230 (1916).

[11] Proc. Roy. Soc., 120A, 217 (1928).

[12] Cf. Rothmund: Rec. Trav. chim., 44, 332 (1925); Barnitt, Derr and Scripture: Ind. Eng. Chem., Anal. Ed., 2, 357 (1930).
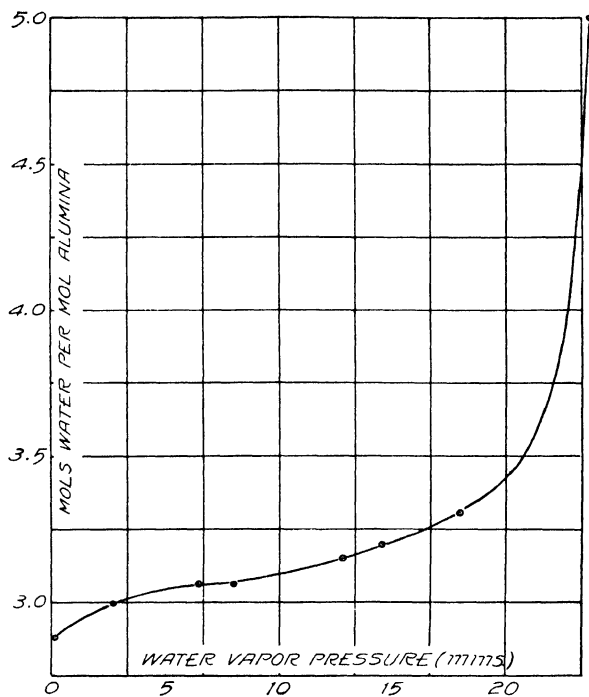
FIG. 2
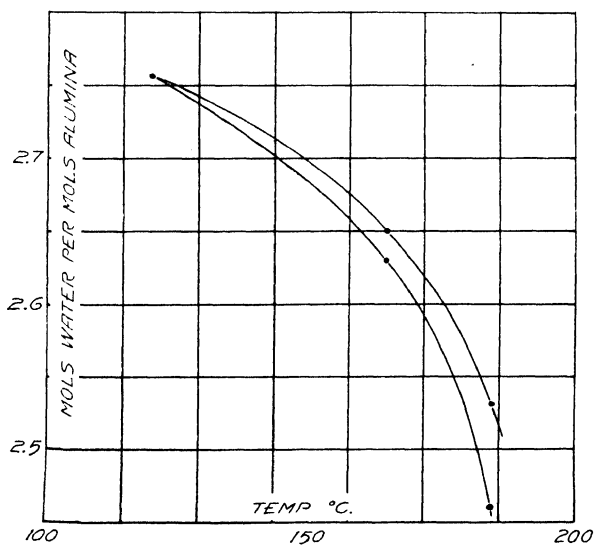
FIG. 3

having a low water vapor pressure was passed over the trihydrate at 119°, a constant composition was reached at least in 96 hours, as shown in Table IV. If the assumption be made that equilibrium was reached at all higher temperatures in ninety-six hours as far as decomposition without lattice rearrangement goes, then any weight change after this must have been due to the ordinary type of hydrate decomposition, with lattice rearrangement. The
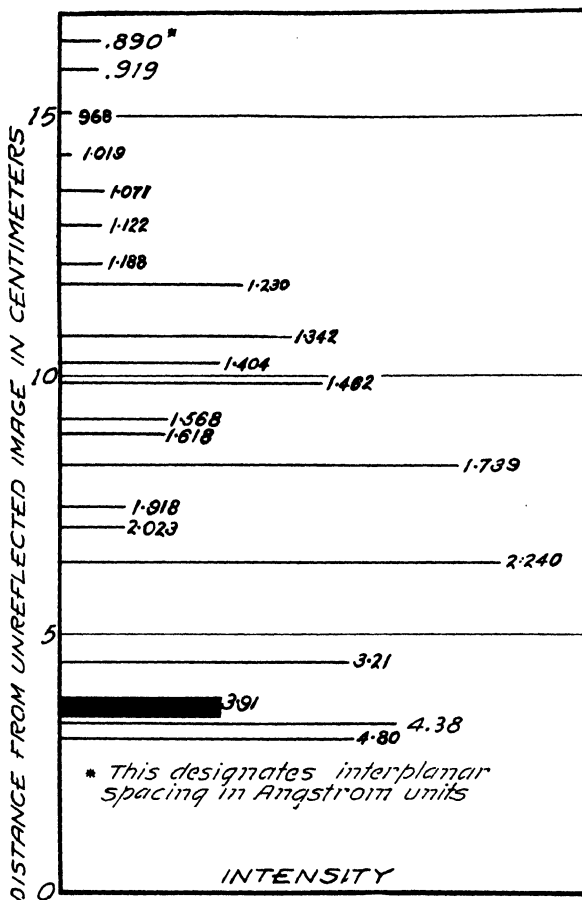
FIG. 4

lower curve of Fig. 4, showing the composition at each temperature after 96 additional hours, is seen to diverge steadily from the upper curve as the temperature increases. The vertical thickness of this band defined by the two curves may thus be taken as an approximate measure of the rate of the ordinary type of hydrate decomposition at the various temperatures. It appears to be almost immeasurably slow at 119°, but much faster at 184°, as would be expected. This will only be an approximation, since the time which elapses between the start of surface dehydration and the start of lattice rearrange-

ment is unknown, and since the rate at any temperature will depend on many factors, some of which were not constant in this experiment, such as composition.

Thus this trihydrate of alumina, and probably hydrates and related compounds in general, may be considered to have two vapor pressures. One is the pressure exerted by water as it evaporates from the surface of the crystal
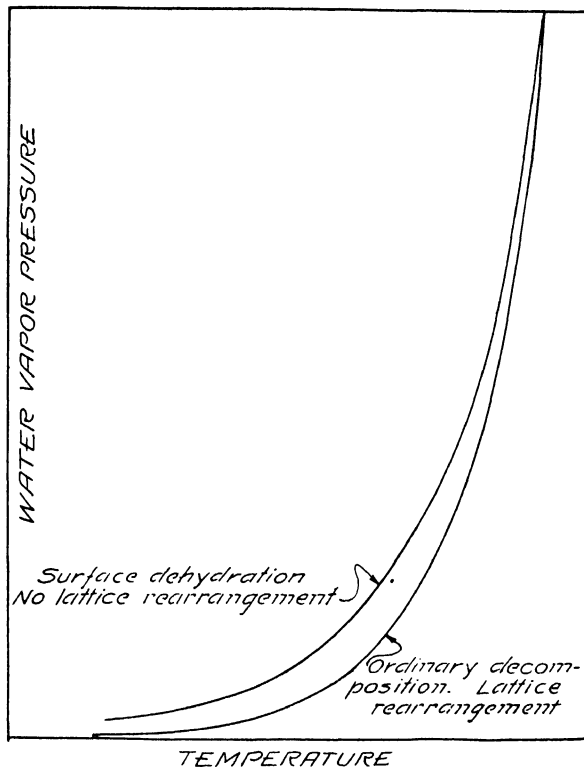
FIG. 5

leaving behind a skeleton lattice structure. From Fig. 2 this is about 2.5 millimeters in the case of crystals of the trihydrate compound at 25°C. The other is the ordinary type of hydrate decomposition pressure depending on the presence of two solid phases. At room temperatures this must be a small fraction of a millimeter for the trihydrate compound. The two pressures probably approach each other as the temperature increases, becoming identical at the transition point, as shown in Fig. 5. The pressures along the upper curve cannot be measured by the ordinary methods used to measure vapor pressure, since they probably decrease as water leaves from deeper and deeper portions of the lattice. These pressures must be measured by some such method as described in this paper.

This conception leads to a promising dehydration theory, which apparently embraces all classes of hydrate decompositions. In brief this theory is that

the vapor pressure of perfect crystals of a hydrate, indicated at different temperatures by the upper curve of Fig. 5, diminishes as water molecules leave from the surface layers until the corresponding point on the lower curve is reached. At this point the outermost portion of the skeleton lattice structure will become unstable, a rearrangement starting at various points and spreading over the surface. The rate at which this rearrangement will penetrate into the crystal will be governed in most cases by the rate of formation of new skeleton lattice within the crystal. The term skeleton lattice is of course used in a relative sense, and does not necessarily imply the total absence of water. For hydrates near their transition point, such as the decahydrate of sodium sulfate at room temperatures, comparatively little water would be lost by surface dehydration before lattice rearrangement would begin. For hydrates at temperatures considerably below their transition temperature, such as hydrargillite, magnesium perchlorate trihydrate, the zeolites, and many others at room temperatures, the skeleton lattice must be a much more stable affair, and comparatively large amounts of water could be lost from the surface without lattice rearrangement taking place. This theory is being investigated at the present time, and will be reported on more fully at a later date.

The conception of a relatively rigid skeleton lattice in which water of crystallization has some freedom of movement is not new. Thus the decomposition of the zeolites has been explained in this manner.[13] Hüttig uses it to explain certain types of hydrate decomposition curves,[14] and Hackspill and Kieffer[15] employ it in their hydrate classification scheme. The possibility of this type of water loss from the surface has not been taken into account by Willstätter and his co-workers,[16] however, in their attempted identification of new hydrates in gels and small particle preparations. In working with alumina preparations two methods were used in obtaining the so-called hydrates: removal of surface water by washing with acetone and determination of the breaks in temperature-composition curves. Both of these methods are open to the same criticism, namely, failure to take into account possible loss of water by surface dehydration in preparations having an enormous surface. Thus in the acetone-drying experiments, any point on a curve similar to or even steeper than that shown in Fig. 2 might be reached, depending on the length of washing and the dryness of the acetone; only by chance could one arrive at the correct formula by this method. In drying preparations like these at increasing temperatures, the loss of water by surface dehydration might be very great, or the water adsorption might be very great, depending on the temperature and the water vapor pressure of the air used in the drying. Again, the correct formula could be obtained only by chance.

[13] See Weigel: Centr. Min. Geol., 1922, 164-78, 201-8; Chem. Abst., 17, 3151 (1923).

[14] Fortschr. Chem. Physik physik. Chem., 18, 5 (1924).

[15] Ann. Chim., (10) 14, 227 (1930).

[16] Ber., 56, 149, (1923); 57, 58 (1924); 58 2448, 2458 (1925); 64, 1697 (1931).

Summary

1. Evidence has been given showing that alumina trihydrate loses water at ordinary temperatures by a surface dehydration in which the remaining lattice structure does not appreciably rearrange.

2. A tentative dehydration theory has been advanced.

3. The methods employed by Willstätter and co-workers to identify hydrates have been criticised as giving doubtful results in the case of gels and precipitates of small particle size.

THE VELOCITY OF SOUND IN SOLUTIONS OF BENZENE AND N-BUTYL ALCOHOL IN N-HEPTANE*

BY E. BRIGHT WILSON, JR., AND WILLIAM T. RICHARDS

Introduction

The velocity of sound v in an elastic medium of density ρ is connected with its adiabatic compressibility β_s by the relation

$$v^2 = 1/\beta_s\,\rho$$

Measurements of the velocity of sound can, therefore, supply one of the coefficients necessary to define the thermodynamic properties of the medium. Owing to the work of Hubbard and Loomis,[1] the accuracy of such measurements in liquids has been greatly increased and it appears probable that interesting information may now be obtained in certain types of liquid systems. In order to explore the field of binary liquid mixtures the measurements reported below were undertaken. Smyth and Stoops[2] have carried out density and polarization determinations for n-heptane–n-butyl alcohol solutions finding that, although the density-composition curves are regular, the polarization shows irregular dependence on composition. These mixtures were, therefore, investigated in order to ascertain whether the behavior of their polarizabilities was to any extent mirrored in that of their adiabatic compressibilities. Benzene–n-heptane mixtures were also measured to give a comparison with a semi-ideal solution.

Experimental Part

Apparatus. The velocity of sound was determined by means of the sonic interferometer which has been devised by Hubbard and Loomis (loc. cit), a cell of the type described by Freyer, Hubbard and Andrews[3] being employed. The quartz crystal, which was entirely similar to that used by the investigators previously cited, was driven by a heterodyned oscillator of the Hubbard and Loomis design. An oscillator of the thermo-galvanometer type was found on the whole more troublesome to operate and no more accurate than the heterodyne. Measurements made at 500.00 k.c. and at 390.07 k.c. were indistinguishable within experimental error, and are hence quoted indiscriminately in the tables which summarize the results. This shows not only the expected independence of the velocity of sound with frequency over a small range, but also the more important freedom of the measurements from errors due to irregularities in the sound wave pattern.

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[1] Hubbard and Loomis: Phil. Mag., **5**, 1177 (1928); Loomis and Hubbard: J. Opt. Soc. America, **17**, 295 (1928).

[2] Smyth and Stoops: J. Am. Chem. Soc., **51**, 3312 (1929).

[3] Freyer, Hubbard and Andrews: J. Am. Chem. Soc., **51**, 759 (1929).

The cell in which measurements were made was immersed in a constant temperature bath held at 25.0°, 35.0° or 50.0°C. to 0.01°, 0.03° or 0.1°C., respectively. The temperatures were determined by means of Beckmann thermometers, which were calibrated by certified Bureau of Standards thermometers.

Materials. The n-heptane was obtained in a pure condition from the Ethyl Gasoline Corporation. It was distilled, refluxed over sodium wire, and finally redistilled, the fraction having a corrected boiling point of 97.0°C. being employed. The index of refraction of this sample for the D sodium lines was 1.38777 at 20°C.

The n-butyl alcohol was refluxed with fresh lime at 100°C. for 12 hours, and then at boiling for 1 hour. It was then left over fused potassium carbonate for a month and distilled. The fraction used had a corrected boiling point of 117.65–117.85°C. and a refractive index of 1.3994.

The benzene was a guaranteed C.P. brand. Since the benzene–n-heptane solutions were employed merely as a standard and since the velocity of sound in this benzene was in good agreement with that found by Freyer, Hubbard and Andrews, it was subjected to no further purification.

TABLE I

The Velocity of Sound in n-Heptane–Benzene Solutions

		Mole fraction benzene			
Temperature °C.		0	0.3040	0.5991	1.0000
25.0		1130	1154	1191	1302
35.0	v in	1087	1109	1147	1254
50.0	m. sec⁻¹	1025	1043	1080	1187

TABLE II

Velocity of Sound and Related Properties in n-Butyl Alcohol–n-Heptane Mixtures

	M. F. Alcohol .2570			M. F. Alcohol .4843		
Temp.	v in m. sec.⁻¹	Density	β_s in bar⁻¹ $\times 10^{10}$	v in m. sec.⁻¹	Density	β_s in bar⁻¹ $\times 10^{10}$
25.00	1139	.7004	1.100	1155	.7252	1.034
35.0	1095	.6917	1.206	1113	.7161	1.127
50.0	1031	.6788·	1.386	1053	.7034	1.282

	M. F. Alcohol .7457			M. F. Alcohol .8243		
25.00	1190	.7603	.929	1205	.7735	.890
35.0	1148	.7519	1.009	1167	.7656	.959
50.0	1088	.7392	1.143	1113	.7526	1.073

	n-Butyl Alcohol			n-Heptane		
25.00	1245	.8061	.800	1130	.6793	1.153
35.0	1205	.7987	.862	1087	.6708	1.262
50.0	1156	.7867	.951	1025	.6575	1.448

The solutions were made up by weight with suitable precautions against changes in composition due to evaporation. It is estimated that their composition was known to better than 0.04 mole per cent.

Measurements. Since the velocity of sound is obtained by simple multiplication from the readings of a micrometer screw, it is possible to give the results of the measurements in the form of self-explanatory tables. Velocities are expressed in meters per second.

Discussion

The measurements in pure benzene are in excellent agreement with those of Freyer, Hubbard and Andrews.[3] Those in n-heptane are consistently lower, indicating, perhaps, that the liquid here under consideration was slightly more dry than theirs. In any case the divergence is hardly greater than experimental error, and certainly cannot affect the present thermodynamic significance of the velocity of sound measured at these frequencies.

In both solutions the velocity of sound is a regular and very similar function of both temperature and composition. Whether each of the two obeys the law of ideal mixtures for this property cannot be determined until the remaining thermodynamic coefficients have been measured. It is already apparent, however, that factors which may gravely affect the regularity of polarization-composition-temperature relationships are without important influence on the velocity of sound. It follows by inference that the adiabatic compressibility may be a property of little interest in the study of binary mixtures, although many more instances are necessary before this can definitely be stated. If the specific heats of these solutions were known it would be possible to state whether any of the first thermodynamic coefficients showed parallel variation with that of the polarizability. Such parallelism, while not to be expected, would be of considerable descriptive interest if it were established.

We are indebted to Professor J. C. Hubbard for supervising the construction of the interferometer cell, and to Mr. A. L. Loomis for the loan of the quartz crystal.

Summary

The velocity of sound in solutions of benzene and n-butyl alcohol in n-heptane at 25, 35 and 50°C. has been measured over the entire concentration range. In both cases it is a regular function of temperature and composition.

Princeton, New Jersey.

THE LIQUID-VAPOR INTERFACE*

BY J. L. SHERESHEFSKY

While the structure of surfaces of solids and of insoluble films is fairly well established, the structure of liquid surfaces in contact with their own saturated vapor remains obscure to the present day. The Laplacian theory of surface tension assumes a uniform density of the liquid up to the vapor phase; on the other hand the theory of van der Waals involves the assumption of a continuous transition from liquid to vapor. Neither of the theories allows for an evaluation of the thickness of the transitional region except on the introduction of an arbitrary potential function.

The experimental evidence seems to be in favor of an abrupt change. Lord Rayleigh[1] found that the reflected light from a clean liquid surface is plane polarized, indicating a definite transition from liquid to vapor. Although Raman and Ramadas[2] found some ellipticity in the polarized light reflected from a clean surface of water, they agree with Rayleigh that the transition layer is about one molecule thick.

The conflict between the theory of van der Waals, which maintains the presence of a non-uniform capillary layer, and the experimental evidence may be more apparent than real. In a previous paper[3] the author has shown that the free surface energy of a liquid surface is the resultant of two effects, one due to the liquid surface proper, and the other due to the vapor phase in contact with this surface. It may therefore be that closely approaching the liquid surface there is an adsorbed phase of vapor which, while being more dense than the rest of the vapor phase, is yet not dense enough to constitute a continuation of the liquid phase. It is this adsorbed phase together with the unimolecular transition layer of the liquid phase that make up the capillary layer, which is giving rise to the various capillary phenomena.

Adsorption of Vapor at a Liquid-Vapor Interface

In a previous paper the author has shown that the surface tension of a liquid may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \tag{1}$$

where σ is the surface tension measured, σ_1 the surface tension of the liquid surface proper, and σ_2 the surface tension of the vapor. From this it follows that the surface tension of a liquid in contact with undersaturated vapor would be higher, and in contact with supersaturated vapor would be lower than

* Contribution from the Chemical Laboratory of Howard University.
[1] Phil. Mag., **33**, 1 (1922).
[2] Phil. Mag., **3**, 220 (1927).
[3] J. Phys. Chem., **35**, 1712 (1931).

ordinarily. In general, a liquid at any given temperature may exhibit various surface tensions depending on the degree of saturation of the vapor in contact with it. Mathematically we may express this by differentiating equation (1) with respect to σ_2

$$d\sigma = -d\sigma_2 \qquad (2)$$

But since σ_2 was shown[1] to be given by the expression

$$\sigma_2 = \frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} \rho_2 \qquad (3)$$

we obtain by differentiating with respect to ρ_2, the density of the vapor, the following differential equation

$$d\sigma = -\frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} d\rho_2 \qquad (4)$$

where the change of surface tension of a liquid with the density of the vapor is given as a function of the critical constants and temperature.

Now since the change in the surface tension is negative, there must be a region contiguous with the liquid surface proper which is richer in vapor than the rest of the vapor phase. Therefore a liquid in contact with its saturated vapor may be represented as a system consisting of three phases, one liquid, one vapor, and one intermediate adsorbed phase.

To calculate the amount of vapor adsorbed in this intermediate phase we may apply Gibbs' adsorption equation. This system, since it has only one component, represents the simplest case to which Gibbs' equation may be applied. Up to the present it has been applied to systems having at least two components, and in order to evaluate the amounts adsorbed, approximating assumptions had to be made. Thus in calculating the adsorption of alcohol at the surface of an alcohol-water mixture Schofield and Rideal[2] used only an approximate equation of Gibbs

$$d\sigma = -\Gamma d\mu \qquad (5)$$

instead of the full equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \qquad (6)$$

where the subscripts (1) and (2) refer to the components of the system. In the case of a liquid in contact with its vapor no error is introduced by using equation (5), since there is only one component in the system.

Since μ, the thermodynamic potential, is given by the expression

$$\mu = \mu_0 + RT\log a \qquad (7)$$

then at a given temperature

$$d\mu = RT\, d\log a \qquad (8)$$

where a is the thermodynamic concentration of the vapor in the vapor phase, which may be substituted by the density of the vapor, ρ_2.

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[1] Loc. cit.
[2] Proc. Roy. Soc., **109A**, 61 (1925).

Combining (8) and (5), Gibbs' equation becomes

$$d\sigma = - \Gamma RT \, d \log \rho_2 \qquad (9)$$

which, when combined with equation (4) gives the final expression for the calculation of the adsorption in the capillary phase, namely

$$\Gamma = \frac{\Delta}{R} \cdot \frac{T_c}{T} \left(\frac{\rho_2}{\rho_c}\right)^{1/3} \left(\frac{\rho_2}{M}\right)^{2/3} (1 - T/T_c)^{0.9} \qquad (10)$$
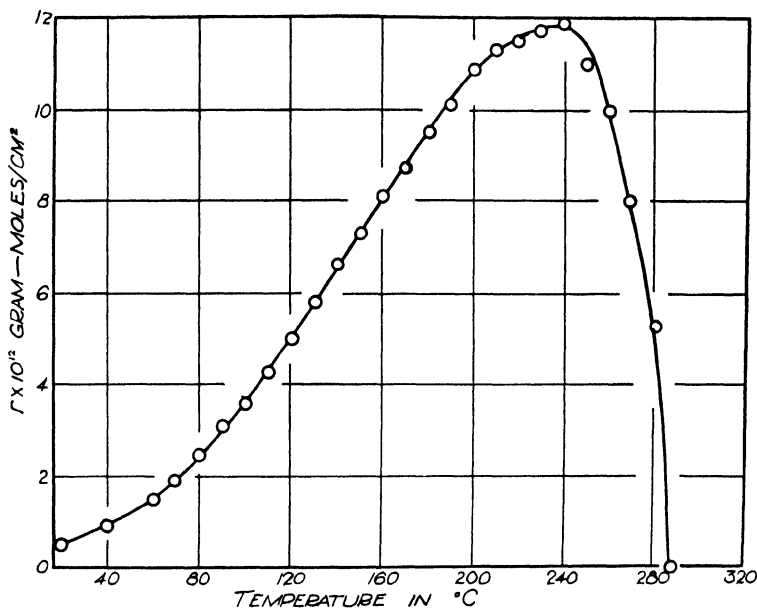
FIG. 1

Adsorption of Benzene Vapor at a Liquid Benzene Surface

It is rather of interest to point out that in combining equations (10) and (3) we obtain

$$\sigma_2 \, 1/\Gamma = RT \qquad (11)$$

which is the so-called equation of state of gaseous films, since σ_2 represents the surface tension lowering, and $1/\Gamma$ is the area occupied by a gram-molecule.

In Table I are given the results of calculations on the adsorption of benzene vapor. In the first column are given the temperatures, and in the second column the corresponding vapor densities, which were taken from the International Critical Tables. In the fourth column are given the amounts adsorbed in gram-mols per square cm. These values seem to be quite reasonable, since alcohol which causes a lowering of surface tension a hundredfold is adsorbed at the surface of an alcohol-water solution in the order of 1×10^{-10} gram-mols per square cm. Fig. 1 shows the variation of adsorption with temperature.

It is of interest to point out that the temperature at which adsorption is at a maximum corresponds to the temperature of maximum surface tension of the vapor. This was to be expected, since the maximum surface tension of the vapor corresponds to a maximum lowering of the surface tension of the liquid surface. This maximum point was shown by the author in a previous paper[1] of this series to be, for all vapors, at 0.9 of the critical temperature. Furthermore, a glance at equation (10) will show that at corresponding temperatures the adsorption of various vapors is proportional to $(\rho_2/M)^{2/3}$, or that Γ $(M/\rho_2)^{2/3}$, which may be called the molar adsorption, is the same for all vapors. The molar adsorption at various temperatures is given in the last column of Table I, and is represented graphically in Fig. 2.

TABLE I

Adsorption of Benzene Vapor at a Liquid Benzene Surface

$\Delta = 1.39$ Mol. Wt. $= 78.05$ $T_c = 561.5$ $\rho_c = .3045$

t°C	ρ_2	$1 - T/T_c$	$\Gamma \times 10^{12}$ gram-mol./cm²	$\Gamma(M/\rho_2)^{2/3} \times 10^9$ gram-mol.
20	.0004	.478	.53	1.79
40	.0008	.443	.93	1.97
60	.0015	.407	1.51	2.11
70	.0020	.390	1.91	2.18
80	.0027	.372	2.43	2.26
90	.0036	.353	3.12	2.43
100	.0047	.337	3.50	2.35
110	.0060	.318	4.27	2.36
120	.0077	.302	5.04	2.37
130	.0096	.282	5.78	2.34
140	.0118	.265	6.61	2.33
150	.0144	.247	7.34	2.26
160	.0173	.228	8.05	2.18
170	.0209	.212	8.75	2.12
180	.0249	.193	9.55	2.04
190	.0298	.176	10.10	1.92
200	.0355	.157	10.80	1.83
210	.0421	.140	11.25	1.70
220	.0502	.122	11.50	1.54
230	.0598	.105	11.72	1.40
240	.0714	.086	11.90	1.26
250	.0855	.068	11.00	1.03
260	.1038	.052	10.00	.83
270	.1287	.033	8.08	.58
280	.1660	.016	5.23	.32
288.5	.3045	0	0	0

[1] J. Phys. Chem., **34**, 1947 (1930).
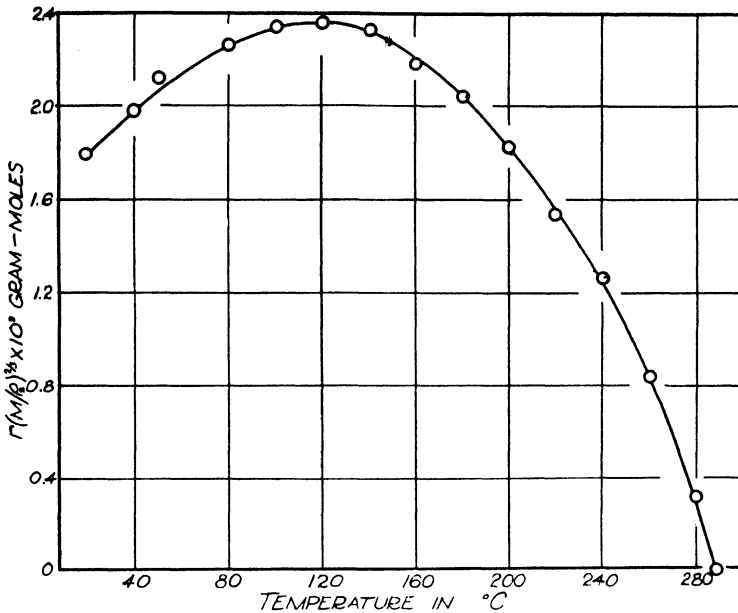
Fig. 2

Molar Adsorption of Benzene Vapor

The Thickness of the Adsorbed Phase

The adsorption of the vapor may be looked upon as due to an attractive force exerted by the molecules in the liquid surface.   Since molecular forces diminish rapidly with distance, the concentration of the adsorbed phase is greater at a distance near the liquid surface, then it rapidly decreases until it approaches the concentration of the vapor phase.   The distance from the vapor phase to the closest approach of the adsorbed molecules to the liquid surface may be termed as the thickness of the adsorbed layer.   If c is the concentration of this phase, which we assume to be approximately uniform, and c_0 is the concentration of the vapor phase, the work done in bringing a molecule from the vapor phase to the adsorbed phase is given by the Maxwell-Boltzmann equation

$$c = c_0 \, e^{\phi/\kappa T} \tag{12}$$

where ϕ is the change in the potential energy of the molecule, T the temperature, and κ Boltzmann's constant.   The energy change, θ, involved in the transference of a gram-molecule is given by

$$c = c_0 e^{\theta/RT} \tag{13}$$

where R is the gas constant.

Since Γ is the number of moles adsorbed per unit surface and d is the thickness of the layer, the amount adsorbed per cubic centimeter is Γ/d and is given by

$$\Gamma/d = c - c_0 \tag{14}$$

when c and c_o are expressed in moles per cubic centimeter. Combining equations (13) and (14) we obtain

$$\Gamma/d = c_o e^{\theta/RT} - c_o \tag{15}$$

or

$$\Gamma/c_o = d\ e^{\theta/RT} - d \tag{16}$$

which relates adsorption with the work of adsorption and the thickness of the capillary layer.

When θ is large d may be neglected, and the above equation becomes

$$\Gamma/c_o = d\ e^{\theta/RT} \tag{17}$$

which in logarithmic form is

$$\frac{\theta}{RT} = \log_e \frac{\Gamma}{c_o} - \log_e d \tag{18}$$

or

$$\frac{.434\theta}{RT} = \log_{10} \frac{\Gamma}{c_o} - \log_{10} d \tag{19}$$

In the range of temperatures where θ and d are constant, plotting log Γ/c_o against $1/T$ should give us a straight line whose slope is $.434\theta/R$ and whose intercept on the log Γ/c_o axis is log d. Since Γ obtained in the preceding part is over a wide range of temperatures up to the critical, and since θ and d surely vary with the temperature of the liquid surface, a straight line could not be expected. However, at lower temperatures we may expect the values of θ and d to remain approximately constant. It is to this range of temperatures that equation (19) is applied.

Fig. 3 shows the curve obtained by plotting log Γ/c_o as ordinate and $1/T$ as abscissa. Table II gives the calculated data for the plot. In the first column are given the values of Γ/c_o, which were obtained from

$$\Gamma/c_o = \frac{\Gamma M}{\rho_2}$$

where ρ_2 is the vapor density and M is the molcular weight. Γ was taken from Table I. In the fifth and sixth columns are given the value of θ and the value of d.

As evident from the figure, the curve is practically a straight line from the melting point, which is for benzene 5.4°C, up to 70°C. The boiling point of benzene is about 80°C. It may be asserted, therefore, that under atmospheric pressure the work of adsorption and the thickness of the capillary layer are practically constant throughout the whole range of temperatures under which the substance is in the liquid state.

In spite of the various approximations introduced into the equation (19), the thickness d obtained is of the right order of magnitude. However, it is much less than the diameter of a benzene molecule as calculated from the density at 20°C. The thickness of the adsorbed layer is evidently not more than one molecule.
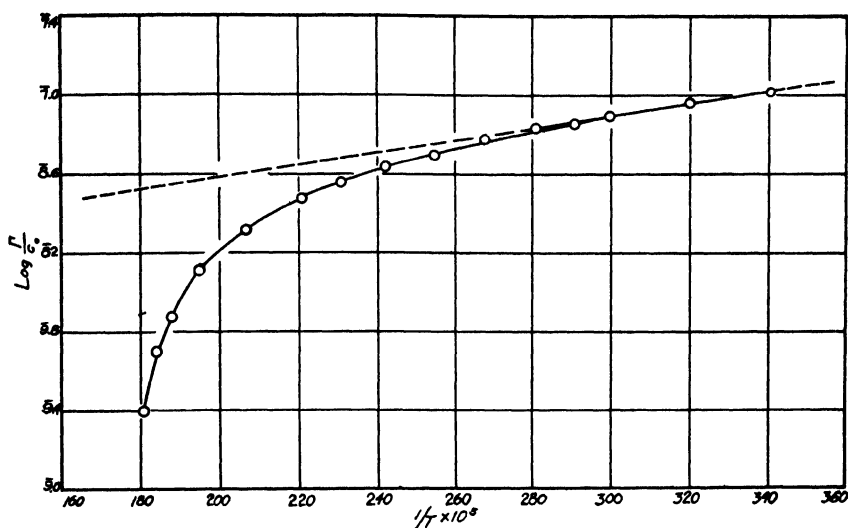
FIG 3

The Thickness of the Capillary Layer

TABLE II

The Thickness of the Capillary Layer

$(\Gamma/c_0) \times 10^9$	$\log(\Gamma/c_0)$	$\dfrac{I \times 10^5}{T}$	$.434\ \theta/R$	θ cal/mole	$d \times 10^8$cm
104	$\bar{7}.0170$	341	298	1365	1.0
90.7	$\bar{8}.9576$	320	298	1365	1.0
78.7	$\bar{8}.8960$	300	298	1365	1.0
74.0	$\bar{8}.8692$	291	298	1365	1.0
69.2	$\bar{8}.8401$	283	298	1365	1.0
67.6	$\bar{8}.8299$	276			
51.2	$\bar{8}.7093$	255			
43.7	$\bar{8}.6405$	242			
36.4	$\bar{8}.5611$	231			
29.9	$\bar{8}.4957$	221			
21.0	$\bar{8}.3222$	207			
13.1	$\bar{8}.1173$	195			
7.5	$\bar{9}.8751$	188			
4.9	$\bar{9}.6902$	184			
2.5	$\bar{9}.3979$	181			

TABLE III

The Density of the Adsorbed Phase

Temperature °C	Density of Vapor ρ_2	Density of Adsorbed Phase ρ	Density of Liquid ρ_1
20	4×10^{-4}	4.16×10^{-3}	.8790
40	8×10^{-4}	7.15×10^{-3}	.8576
60	15×10^{-4}	11.78×10^{-3}	.8367
70	20×10^{-4}	14.78×10^{-3}	.8248

In Table III are given the densities of benzene in the three co-existing phases. The density of the adsorbed phase was calculated by means of Boltzmann's equation

$$\rho = \rho_2\, e^{\theta/RT}$$

in which θ was taken to equal 1365 calories per gram-molecule. A comparison of the densities in the three phases shows that, while the density of the condensed phase is from seven to ten times greater than the density of the vapor phase, the former is from sixty to two hundred times smaller than the density of the liquid. The transition from the liquid to the adsorbed phase may therefore be considered to be abrupt, and the light reflected from the liquid surface would be plane polarized, in accordance with the experiments cited above.

Summary

Evidence as to the thickness of the capillary layer of liquid surfaces is reviewed.

It is suggested that contiguous to a liquid surface there is an adsorbed layer of vapor.

An equation was derived whereby the amount of adsorbed vapor may be calculated.

It is shown that at corresponding temperature the "molar adsorption" is the same for all vapors.

The work of adsorption and the thickness of the capillary layer is calculated by applying the Maxwell-Boltzmann law.

Washington, D. C.,
January, 1932.

A TEMPERATURE CONTROL CLOSET
FOR ADIABATIC CALORIMETRY*

BY B. CLIFFORD HENDRICKS AND WARREN H. STEINBACH, JR.

In a former communication[1] one of us and others reported a temperature control closet constructed of wallboard. This closet later proved quite unsatisfactory when work with it was attempted during summer months with atmospheric temperatures at levels ten or more degrees above the twenty degree level then in use in the calorimeter. Later, when it was decided to use a twenty-five degree temperature for the constants being determined, the wallboard arrangement was entirely inadequate for either summer or winter.

Help in remodeling the wallboard structure into something more permanent and dependable was not easily found. Publications[2,3] upon calorimetry refer to such controls but give no details either of construction or of operation. Isabe[4] describes a toluene-mercury thermo-regulator in circuit with a relay which is said to establish thermal constancy to $0.05°C$. in an air chamber whose dimensions are not given. A more recent paper[5] describes a double walled room equipped with a temperature control which raises temperature by electric heating units, decreases it by water coils and equalizes it by electric fans.

For adiabatic work the atmospheric temperature does not need to be thermostated but rather must be under such control by the experimenter that increases or decreases in its value may be made at a rate known in advance of their use. In order to maintain a temperature varying, either positively or negatively, from that of the laboratory temperature, provision has to be made for: 1) heating, 2) cooling, 3) insulation from the room, and 4) the manipulation of all experimental equipment within it by outside controls. To meet these requirements, the closet shown in Fig. 1 was made and has been in use in this laboratory for the past two years.

The closet is constructed of soft wood and has the dimensions 185 by 70 by 65.5 cm. The bottom is raised 20 cm. above the floor. The earthen-ware jar, J, of 120 liters capacity, is installed in the lower half of the cabinet, by removing screws which hold panel doors in place. The upper half is provided with two hinged doors, one front and one back, with glass windows, W', W'', through which all observations are made. During all experiments these doors

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* Contribution from the Chemical Laboratory of the University of Nebraska.

[1] B. Clifford Hendricks, James H. Dorsey, Royce LeRoy, and A. G. Moseley, Jr.: J. Phys. Chem., **24**, 418-426 (1930).

[2] Frederick Barry: J. Am. Chem. Soc., **42**, 1915 (1920).

[3] W. P. White: "The Modern Calorimeter," 20, 45 (1928).

[4] Hajime Isabe: J. Chem. Soc. Japan, **43**, 650-3 (1922).

[5] U. R. Evans: Chem. and Ind., **50**, 66 (1931).

are kept closed, yet temporary changes in equipment within the closet may be quickly made by merely opening them.

Provision is made for stirring the contents of the calorimeter vessel, inserted at Ga, the calorimeter water jacket in J, and the air in the upper part of this closet, through fan F, by means of power through a system of pulleys, P, P', S', S'', S'''.

In those experiments in which heat is evolved, giving an elevation of temperature above that of the 25 degree level of the bath, adiabatic work requires that bath, water jacket, and air closet temperatures must be brought upward at a rate comparable with the change taking place in the calorimeter. The range of this change, for which this apparatus was constructed, was assumed to never be greater than two degrees on the Centigrade scale. All] tests here reported are made for that range.

The water jacket is equipped with a mercury-toluene thermo-regulator in series with a polarized relay. This thermo-regulator can be thrown into circuit with any one of the two 250-watt lamps or the two 250-watt knife heaters, each immersed in a different quadrant of the water jacket, and by test was found to maintain temperature constancy at Ga, Fig. 1., to 0.004 degrees C. By hand control any one of the four heaters raises the temperature of the water jacket above 25 degrees C. at a rate of 0.04 degrees per minute.

FIG. 1

Temperature elevation of the air closet is accomplished by a lamp at L. Tests indicate that a 50-watt lamp in this position on a 110-volt circuit, raises the air temperature at the rate of 0.1 degrees C. per minute when the water-jacket temperature is 25 degrees C. and room temperature 24 degrees C. A more powerful or less powerful lamp shows correspondingly faster or slower rates of temperature change.
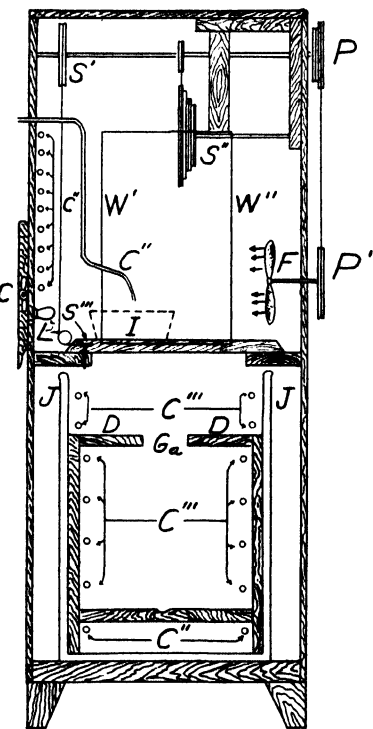
In heats of solution experiments, where heat is commonly absorbed, calorimeter temperatures drop below the water jacket level. Richards and co-workers[1] met such an emergency by the introducing of ice water into the water jacket. In case slower cooling is adequate ordinary hydrant water[2] has been put into the water jacket. The apparatus here presented uses neither

[1] T. W. Richards: Proc. Am. Acad., 38, 434 (1920).

[2] B. Clifford Hendricks, James H. Dorsey, Royce LeRoy and A. G. Moseley, Jr.: J. Phys. Chem., 24, 419 (1930).

of these cooling methods. Inside of the water jacket jar, J, arranged in spirals, with seven turns, are 1160 cm. of three-eighths inch copper tubing, C'''. This tubing is connected at one end through a closed-end manometer to the laboratory water and the other end projects into a sink. A compression faucet permits the adjustment of the water pressure of the entering water to almost any desired value. A series of tests[3] made it possible to prepare a calibration curve showing manometer pressure reading plotted against the rate of cooling. These values vary from a rate of 0.007 degrees C. per minute with a manometer pressure reading of five centimeters to a cooling rate of 0.186°C. per minute when the pressure reading is 18 cm. The entering tap water was at 15.5°C. during the tests. By reference to the calibration curve the experimenter can set the pressure through those coils to duplicate any rate of cooling desired between the limits named. The flow of water through the coils may be deflected from them by merely turning the two-way stop cock, C.

A similar control of the air temperature of the closet is sought by running water through coils, c'. However, these coils do not show any marked increase in speed of cooling as the pressure of the water through them is increased. After but a few minutes of water flow through them they become wet with condensed moisture. This condensation assumes, after a very short time, such proportions that it is necessary to provide drains to carry it away. It seems reasonable to assume that it is responsible for the reduced cooling when the water flow through the pipes is increased. Tests indicate that the coils may be depended upon to cool the air space of the closet at the rate of .13°C. per minute with the temperature one degree above the water jacket temperature and two degrees above room temperature. This rate of cooling can be improved by using compressed air through C'' over ice in Pan, I. For this procedure the drop was 0.26°C. per minute. By the addition of salt to the ice the cooling rate was increased to 0.62°C. per minute.

The closet is not air tight but with the doors shut it is not a difficult matter for the experimenter to hold the temperature of the air of the closet to within 0.2°C. of the desired value. While this is maintained by hand control, such control is justified since adiabatic work requires not constancy, but near-equivalence.

In order to introduce samples into the calorimeter after equivalence of its temperature, and the water jacket temperature has been achieved, an electro-magnetic trip was devised. This releases a weight which forces a plunger to push the cap out of a sample tube within the calorimeter. The calorimeter's thermometer is tapped, to prevent mercury from sticking, by a rubber covered hammer of a mutilated electric bell. This is also operated by a switch upon the outside of the closet.

After having fixed the calorimeter in the bath with its sample tube loaded, the electro-magnetic trip and thermometer tapper adjusted, it is possible for the experimenter to start the stirring motor, vary the heating or cooling rate, illuminate the thermometers, release the sample, tap the thermometer, all by means of switches and without opening doors or even moving from his seat.

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[3] The authors wish to credit Mr. R. V. Witter for making these tests.

CANCER RESEARCH

BY B. CRAWLEY

The twenty-ninth annual report of the Imperial Cancer Research Fund states that "though there are many examples of the greater viability of cancer cells as compared with the normal, there is no evidence as yet available of a single property in which they are more vulnerable," and again: "We are not yet in possession of such knowledge of the properties of the cancer cells as would ndicate clearly the direction in which a rational specific therapy of cancer should proceed." It is bitter to have to confess after thirty years' work that as we can't find what is wrong, we don't know how to set about putting it right.

What is to be done next? It is not of much use to go on collecting facts indefinitely without attempting to fit them into a general scheme of some sort. Although (as Dr. Dale has recently pointed out) biologists are traditionally shy of theories on account of the number of unknown and uncontrollable variables always present in their work, and cancer research workers in particular have learnt over and over again how misleading an imperfectly checked hypothesis can be, yet the sheer bulk of undigested observations is becoming so great that even "Chemical Abstracts" may presently fail to encompass it. It is time to sit down and think things over.

In a series of papers appearing in the "Journal of Physical Chemistry" from January 1931 onwards, Professor Bancroft has been amplifying and extending an old suggestion of Claude Bernard's on the nature of anaesthesia. His ideas may be very briefly summarised as follows. The successive cell states of (1) excitation, (2) anaesthesia or temporary inhibition of activity, and (3) death, are respectively characterised by (1) incipient reversible azglomeration (enlargement of the micelles) of the protein sols contained within the cell, (2) a more advanced but still reversible agglomeration, and (3) irreversible coagulation. His theory thus explains why a single chemical reagent, or even suitable radiation or mechanical shock, can under different conditions behave as (1) a stimulant, (2) a narcotic or antiseptic, and (3) a cell poison or disinfectant. The sedative action of bromides, their power of reducing irritability and of counteracting narcosis and anaphylactic shock, together with the catatonic nature of the symptoms produced by excessive use of bromides, he explains as due to the peptising action of the bromide ion on the negatively-charged cell proteins.

Taking Professor Bancroft's theory as a basis, let us suppose —as a working hypothesis—that the essential difference of malignant cells (and possibly of embryonic cells also) from the normal of the same species lies in *their protein sols being in a chronic state of excessive peptisation*, i.e. the micelles are smaller than those occurring in normal cell colloids.

If this hypothesis is correct, the causation of cancer by continued irritation may be explained as follows. After a period during which the cell colloids are maintained in a state of incipient agglomeration (stimulation), and at the same time are called upon to do heavy repair work, sooner or later they become

protectively altered in such a way that the cells perform the abnormal repair work as a part of their customary and heritable duty (malignant growth) without requiring stimulation; in other words, increased peptisation has rendered the protein sols too stable to be appreciably agglomerated by stimuli which have a marked effect upon the sols of similar normal cells. The mechanism of the protective change may possibly be connected with the abnormally rapid breakdown of glucose in cancerous tissue,—for it is not unlikely (Nechkovitch; Archiv int. Physiol., **28**, 285) that glucose in normal tissue fulfils the physiological rôle of maintaining the cell colloids at their optimum dispersion. Then there is the question of susceptibility: why do some persons readily develop malignant growths in response to a given irritation, while others are either resistant for a much longer period or altogether immune? At present we can only reply in general terms that the cell proteins of susceptibles are for some reason unusually prone to incipient agglomeration as the result of irritation, so that they are more readily perverted into the protective peptisation characteristic of malignant growths. This suggests why cancer is largely a disease of later life; with advancing age the cell colloids always tend to become more readily agglomerated, as is evidenced by the easily excited emotions of the aged, by the habit of dozing and falling asleep on the slightest pretext, and by general sensitiveness toward shock.

The hypothesis of excessive peptisation, i.e. abnormal stability towards agglomerating agents, at once accounts for the observation that sarcoma cells exhibit a higher resistance than normal connective-tissue cells to the dyeing action of trypan blue, and may also explain why normal cells fail to form around the boundary of a malignant tumour an impervious coating such as limits the extent of a non-malignant growth. Treatment of malignant growths by intravenous injections of colloidal metals, though dangerous, has shown some positive results, as has also the use of certain bacillus toxins and of emulsions of embryonic tissue; the normal body tissues may be supposed to be stimulated by these agents into a sufficiently enhanced state of activity (incipient agglomeration) to put up a successful fight against the progress of the tumour. Excessive doses of metallic colloids, however, favour instead of retarding the malignant growth, because such a very strong stimulus carries the agglomeration of the normal cell proteins right through to the anaesthetised or inhibited stage, while producing only an exciting effect on the more stable cancer cells. The statement that, in every property which has been experimentally investigated, cancer cells are more resistant to attack than normal cells, becomes of small moment as soon as it is realized that investigation has been confined to one single property, namely the susceptibility of the colloids to agglomeration. Chemical poisons, heating, freezing and other destructive radiations all attain their lethal effects on cells by directly or indirectly bringing about irreversible coagulation of the cell proteins; and since malignant cells happen to resist coagulation more strongly than normal cells, it is easy to understand how a "cure" based on coagulating agents may well prove more fatal than the disease itself.

It remains to be seen what help the hypothesis can give us toward preventing or curing malignant growths. As regards prevention the answer is:

with our existing knowledge, not much. We know that mechanical and chemical irritants are liable to produce cancers, and the means of preventing such cases are self-evident. But cancers often develop without clear evidence of the nature of the primary irritant, so that while it is easy to blame civilized man's general mode of life it would be absurd to hope to exclude thereby every possible cause. Until a new experimental technique has been developed there is no hope of establishing with certainty the exact physicochemical changes which bring about the increased dispersion of malignant cell proteins. Phenomena of antiserum therapy and anaphylaxis, for instance, show that present physical and chemical methods cannot detect the difference between two proteins which are sufficiently dissimilar for one to cause rapid death (coagulation) in all cells of a given species to which it is applied, while the other is quite without effect,—so that, even if a specific cancer toxin existed and could be isolated, little light would be thrown thereby on the mechanism of the disease. Probably, too, there are at least as many separate strains of malignant cells as there are kinds of protein in the normal cells from which they are derived. A study of the chemical structure of extraneous substances which happen to agglomerate cell proteins—constituents of coal tar, for instance—is unlikely in any event to tell us more about the nature of the resulting injury than we might learn about a bruised shin by analysing the wood of the misplaced chair that caused the damage. The hope of attributing the general causation of cancer to a specific molecular structure is quite illusory.

The hypothesis of excessive peptization promises more immediate success in the treatment of existing cancers. There is evidence that a cell's activity can be inhibited not only by excessive agglomeration, but also by peptisation if the latter be carried to extremes; the cancer cell is already abnormally peptised to begin with, and a peptising agent can probably be found which, while increasing the dispersion of normal cell colloids to a certain extent but not enough to interfere seriously with their functions, will disperse the malignant cell colloids to the extreme point necessary for inhibition. Preliminary trials should be made of local treatment with the largest possible doses of negative-protein dispersing agents such as ephedrine, sodium thiocyanate or sodium bromide, mild general stimulants perhaps being administered at the same time to counteract the effect on the normal cells.

To characterize malignant cells by the abnormally dispersed condition of their protein is obviously only one step toward the solution of the cancer problem; the basic hypothesis will have to be added to again and again as we acquire more knowledge of the nature and mutual actions of the various external and internal cell secretions. But even in its present simple form the idea is able to unify a great number of observations, of which only a few have been mentioned in this note. Although we must admit that the cancer problem as a whole "will not yield to the sound of a trumpet," it is equally certain that it will not be solved by outworn technical methods such as the staining of cells before microscopic examination, nor by a habit of thought which is content to tabulate facts without correlating ideas.

Wendover,
Bucks.

PHASE RULE STUDIES ON THE PROTEINS. VI*

Non-Aqueous Solutions

BY WILDER D. BANCROFT AND S. LOUISA RIDGWAY**

Historical

When proteins were found to be amphoteric and to contain amino acids, it was assumed without question that true compounds were formed with the acids and bases which the proteins "bound." The later studies of colloid chemistry and adsorption suggested to some that the mechanism of the "binding" might be adsorption rather than compound formation. Van Slyke and Van Slyke[1] were among the first to mention this possibility. They worked in water solution with casein and such dilute acids that no casein dissolved. They measured the acid left over by a conductivity method. After citing twelve references supporting compound formation between acids and proteins; and after carefully going over their own data with reference to the three possibilities of compound formation, solution of acid in protein, and adsorption, they decided that in their case they had adsorption. T. B. Robertson[2] immediately replied to this article to support the theory of compound formation. For each of the criteria of adsorption set up in the first article, he gave examples of chemical reactions which would fulfill it. Van Slyke and Van Slyke[3] answered Robertson to the effect that their differences were partly a matter of the definition of adsorption, and that their criteria determining adsorption could apply equally well to compound formation which is incomplete, reversible, and occurs between changing proportions of the mass of reactants. They said that proteins might form compounds with acids under other conditions, but that they did not believe they did in their case. Robertson in later works[4] has continued to favor compound formation, and in the latest one cited says: "It is now admitted by all observers who have directed adequate attention to this question that the proteins accomplish the neutralization of acids and bases in stoichiometrical, that is, molecular or equivalent-molecular proportions."

In general, some stand is taken for one theory or the other by the various leaders of protein research and by many colloid chemists. Loeb[5] is one of the

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[1] Am. Chem. J., **38**, 383 (1907).

[2] J. Biol. Chem., **4**, 35 (1908).

[3] J. Biol. Chem., **4**, 259 (1908).

[4] "Die physikalische Chemie der Proteine" (1912); "The Physical Chemistry of the Proteins" (1918); Chapter in Alexander's "Colloid Chemistry", 2 (1926).

[5] "Proteins and the Theory of Colloidal Behavior" (1924).

strongest supporters of the compound theory. He studies proteins from the point of view that they are, at least partially, in true solution and follow the classical laws of stoichiometrical chemistry. He explains physical properties of proteins such as swelling, osmotic pressure, membrane potential, and viscosity on the basis of the Donnan membrane equilibrium, where the non-diffusible ion is a protein ion of a protein salt. This has been criticized by Donnan[1] who says that the Donnan theory rests only on the existence of equilibrium and the existence of certain restraints which restrict the free diffusion of one or more electrically charged or ionized constituents; and that protein with adsorbed acid or basic ions fulfills the second requirement as well as protein ions. Pauli[2] criticized Loeb from a different point of view, namely that there is no restriction of the movement of the particles of protein in solution. He has also been criticized in reviews on his book by Bancroft[3] and by Alexander[4] who feel that his experimental results point as much, or perhaps more, to adsorption than to compound formation.

Procter,[5] Procter and Wilson,[6] Wilson,[7] and Wilson and Wilson,[8] have developed a theory for the swelling of gelatine in dilute acid mathematically based on the Donnan membrane equilibrium and on the assumption that a highly ionized protein salt is formed. Their "chemical combination" would sound very much like adsorption to many chemists for it occurs on colloidal surfaces, is not stoichiometric, and is a function of the concentration of the acid present. They got formulae for both the concentration of the chemically bound electrolyte and the total quantity of electrolyte either combined with or present in the solution in contact with the colloid, as functions of the concentration of the electrolyte in solution. The curves for these functions are approximately the same as those obtained by the use of the ordinary empirical adsorption formula. Here again, Donnan[9] has criticized them in the same way he did Loeb—that proteins with adsorbed ions would give the same results as protein ions. Atkin[10] did work which he thought supported Procter and Wilson. Ghosh[11] confirmed the results of Procter and Wilson on the swelling of gelatine in acid. He derived an equation for the swelling of gelatine on the basis of the Donnan equilibrium, but he made fewer assumptions. He says that it is more likely that acid is adsorbed than combined.

Some of the other workers who in various ways support compound formation are Schmidt, Greenberg, et al.[12] from the University of California,

[1] Chem. Rev., **1**, 87 (1924).

[2] Alexander: "Colloid Chemistry,", **2**, 223 (1926).

[3] J. Phys. Chem., **26**, 687 (1922).

[4] Chem. Met. Eng., **27**, 368 (1922).

[5] J. Chem. Soc., **105**, 313 (1914).

[6] J. Chem. Soc., **109**, 307 (1916).

[7] J. Am. Chem. Soc., **38**, 1982 (1916).

[8] J. Am. Chem. Soc., **40**, 886 (1918).

[9] Chem. Rev., **1**, 87 (1924).

[10] J. Soc. Leather Trades' Chem., **4**, 248, 268 (1920).

[11] J. Chem. Soc., 711 (1928).

[12] J. Biol. Chem., **25**, 63 (1916); J. Gen. Physiol., **7**, 287, 303, 317 (1924-25); **8**, 271 (1925-26); Univ. of Cal. Publications in Physiol., **5**, 289, 307 (1926); **7**, 9 (1927).

Hitchcock,[1] Lloyd and Mayes,[2] and Cohn.[3] Others besides those already mentioned who favor adsorption are Moeller,[4] de Izzaguirre,[5] Shukoff and Stschoukareff,[6] and Fanselow.[7] Tolman and his co-workers[8] have a theory of the swelling of proteins in acid and alkali which is based on adsorption. This adsorption they suppose is of a chemical nature and occurs in the case of acids on the free amino groups and in the case of alkalies probably on enolized —COHN— groups.

Gortner and his associates[9] believe that between pH 2.5 and 10.5 there is true compound formation, and that at a pH above or below these limits, there is true adsorption. They have performed numerous and careful experiments on which they base this belief.

In an effort to distinguish between the two possibilities of compound formation and adsorption, many experiments have been made. Although the supporter of each theory can see proof for his own theory in his experiments, very often his opponent can see proof for the opposite one in the same experiments. Frequently the opponents appear to be separated further than is actually the case by a disagreement in the definition of terms, but there still remain two distinct possibilities, either of which, or both, may take place in a given case. The criteria which distinguish between the two are not sufficiently clear-cut under most of the experimental conditions employed. Bancroft and Barnett,[10] and Belden[11] performed some experiments of such a nature that the results show definitely whether there has been compound formation or adsorption, or both, under the conditions of the experiment in any given case. They treated solid proteins with gaseous HCl and NH_3 in a special apparatus. If a compound formed, the pressure remained constant over the two solid phases as long as they both existed; if an adsorption complex formed, the pressure varied continuously. Casein, arachin, fibrin, gliadin, edestin, and gelatine were found to form compounds with HCl with subsequent adsorption of further acid on the compound formed. Zein simply adsorbed HCl. Casein, zein, arachin, fibrin, gliadin, and gelatine adsorbed NH_3 without any indication of compound formation. This method is obviously not applicable to caustic soda. People might claim that a strong base would react stoichiometrically with the proteins.

Introduction

The present work follows directly that of Bancroft, Barnett, and Belden. We have attempted to extend their method to apply to acids and bases, which

[1] J. Gen. Physiol., 4, 597, 733 (1921-22); 5, 383 (1922-23); 6, 95 (1923-24); 12, 495 (1928-29); 14, 99 (1930-31).
[2] Proc. Roy. Soc., 93B, 69 (1922).
[3] Physiol. Rev., 5, 349 (1925).
[4] Collegium, 319, 382 (1920).
[5] Kolloid-Z., 32, 47 (1923).
[6] J. Phys. Chem., 29, 285 (1925).
[7] Colloid Symp. Mon., 6, 237 (1928).
[8] J. Am. Chem. Soc., 40, 264 (1918); 41, 1503, 1511 (1919).
[9] Colloid Symp. Mon., 2, 209 (1925); J. Phys. Chem., 34, 1071 (1930).
[10] J. Phys. Chem., 34, 449, 753, 1217, 1930, 2433 (1930).
[11] J. Phys. Chem., 35, 2164 (1931).

are not necessarily gases. The acid or base is dissolved in some solvent, chemically inert to the system, which does not dissolve the protein or the product formed. Varying amounts of the acid or basic solution are added to known weights of the protein and sufficient solvent added to make the volume a convenient and definite one. When equilibrium has been reached, some of the supernatant liquid is pipetted off and the excess acid or base determined by titration. From these data the amount of acid or base taken up per gram of protein may be calculated. These values are plotted against the acidity or basicity of the supernatant liquids.

On the basis of the phase rule, we may predict the types of curves which will be obtained, and explain their significance. Suppose first that an adsorption complex forms and there is never more than one solid phase present. There are three components—protein, acid or base, and solvent. There are three phases—one solid, one liquid, one vapor. Then, since $F = C - P + 2$ (where $F =$ the number of degrees of freedom, $C =$ the number of components, and $P =$ the number of phases), $3 - 3 + 2 = 2$. The temperature is fixed at room temperature, using up one degree of freedom. One variable is left—that of the concentration of the liquid phase. If a compound is formed instead of an adsorption complex, there are two solid phases until the protein is entirely used up, and therefore only one degree of freedom in that range. Since the temperature is fixed, there is no variable left. In the presence of two solid phases, then, the composition of the liquid must remain fixed. A smooth, continuously varying, curve indicates adsorption; one with a "flat" showing constant composition for the liquid phase indicates a compound. This method was used with success by Kawamura[1] on stearic and humic acids with NaOH in water.

Preliminary Experiments

Proteins are very complex bodies and there has been much controversy as to the character of their combination with acids and bases. In order to test thoroughly the method outlined above, it was first tried on some solid basic and acidic substances for which the results could be predicted accurately.

1. *Succinic Acid*—It is difficult to find a fairly simple carboxylic acid which is not quite appreciably soluble in any solvent which could be used with proteins. Succinic acid and isobutyl alcohol were chosen as the best available pair although at $25°$ the acid is soluble to the extent of nearly three percent in the alcohol. This is much greater than we should like for a test case, and affects considerably certain portions of the curve. The curve should show two flats corresponding to the mono- and di-sodium salts. There might or might not be adsorption on the latter.

Experimental work on the acid immediately presented a second difficulty. The di-sodium salt formed in such a way as to coat the solids in the system almost completely and to hinder greatly the attainment of equilibrium. The first experiment was carried out with sodium isobutylate in absolute isobutyl alcohol in an effort to cut down the water content of the system and therefore

[1] J. Phys. Chem., **30**, 1364 (1926).

TABLE I

Summary of the Runs on Succinic Acid

Sub-stance No. treated	Base used	Solvent	Time of run	Special treatment*	Result
1. Succinic acid	Sodium isobutylate	Absolute isobutyl alcohol	7 days	W 1 day	Equilibrium not reached
2. "	NaOH	"	3 days	W 2 days	"
3. "	"	"	7 days	W 5 days	Approximate flat for mono salt, then no equilibrium.
4. NaH suc-cinate	"	"	6 days	W 6 days	Equilibrium not reached
5. "	"	"	1½ days	R 22½ hrs.	"
6. Succinic acid	NaOH up to 1 equivalent	95% isobutyl alcohol	1 day	R 18 hrs.	Some ester forma-tion and solution of rest
7. NaH suc-cinate	NaOH	"	5¼ days	R 5¼ days	Flat for di-sodium salt and complete adsorption on it
8. "	"	"	4¼ days	R 2 days	"
9. Succinic acid	"	"	11 days	S 140 hrs.	See Fig. 1. and Table II

* W = warm (at 50°-60° on top of an oven).
  R = refluxed.
  S = shaken in a mechanical shaker. See p. 1303.

the solubility of the succinic acid. From that first trial to the final attainment of the desired results, Table I shows the methods used and their measures of success.

It is obvious that the presence of a small amount of water hastens equilibrium, probably because of the greater solubility of the acid and its salts. The acid sodium succinate was used in order to facilitate the obtaining of the second flat, although it was later found to be unnecessary. It was made by adding standard NaOH to a weighed quantity of succinic acid, evaporating the water, and drying. Its purity was determined by finding the neutral equivalent.

Runs 6–8 in Table I, plotted on the same graph, give a curve of the sort that ought to be obtained, but which still leaves much to be desired. The conditions for the three runs were not the same; and there was considerable ester formation between the refluxing alcohol and the unused acid or acid salt. A final run (No. 9), using succinic acid with NaOH in 95% isobutyl alcohol,

was made.   It stood for eleven days and was shaken in a mechanical shaker about 140 hours of that time.   Equilibrium, as indicated by activity to phenol-phthalein, had been reached in numbers 1–9 in about four days, but time was given for the rest to come to equilibrium.   Ester formation was separately determined to be about 5% in number 1 where it would be greatest.   The results are given in Table II and Fig. 1.
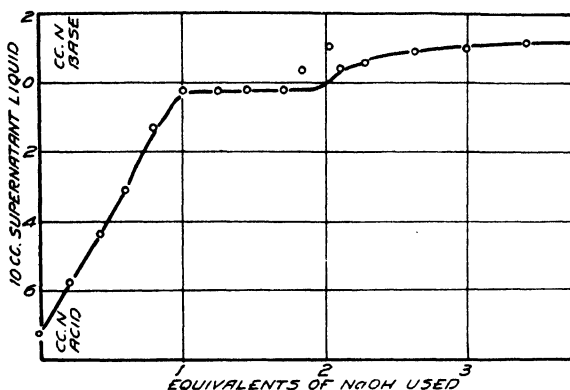
FIG. 1
Succinic Acid and NaOH in 95% Isobutyl Alcohol

TABLE II

Succinic Acid and NaOH in 95% Isobutyl Alcohol

1 gm. succinic acid, which requires 16.94 cc. of N NaOH for complete neutralization, taken for each number

Length of run—11 days

No.	a cc. N NaOH added	b Total vol. of liquid added cc.	c cc. N acid (or base) for 10 cc. sup. liq.	d cc. N base in super. liquid c × b/10	e cc. N base used a − d	f Equiv. of NaOH used e/8.47
1.	0.00	20	7.20 base	—	0.00	0.00
2.	1.80	20	5.77 "	—	1.80	0.21
3.	3.60	20	4.32 "	—	3.60	0.43
4.	4.95	20	3.11 "	—	4.95	0.59
5.	6.75	20	1.30 "	—	6.76	0.80
6.	8.56	20	0.24 "	—	8.56	1.01
7.	10.81	40	0.24 "	—	10.81	1.24
8.	12.61	40	0.24 "	—	12.61	1.46
9.	14.86	40	0.22 "	—	14.86	1.72
10.	17.11	40	0.34 acid	1.36	15.75	1.83
11.	18.97	40	0.32 "	1.27	17.69	2.09
12.	21.55	40	0.53 "	2.12	19.43	2.29
13.	23.42	60	1.04 "	6.26	17.16	2.03
14.	25.86	40	0.90 "	3.60	22.26	2.63
15.	29.31	40	0.99 "	3.94	25.37	3.00
16.	33.62	40	1.13 "	4.54	29.09	3.43

The curve has three distinct parts. From o to 1 equivalent, the curve is a measure of the acid in solution after all the NaOH present has been used. If there had been more acid in proportion to alcohol, there would have been a horizontal line extending some short distance from the vertical axis along which would lie points determined from systems in which both solid acid and sodium acid succinate were in contact with the liquid at equilibrium. Actually we had no such points. From 1 to almost 2 equivalents, there is the flat due to the formation of normal sodium succinate. The sloping portion just before 2 equivalents is due to the slight solubility of the acid salt in the alcohol. The rest of the curve shows adsorption of alkali on the normal salt. The amount of adsorption depends on conditions. In the first curve obtained, it was complete.

2. *Uric Acid*—Although uric acid is not a true carboxylic acid, it was used next because of its very low solubility in alcohol. Its formula is:—

$$
\begin{array}{ll}
\text{HN—C=O} & \text{N=C}^{\text{OH}} \\
\quad|\qquad| & \quad|\qquad| \\
\text{O=C}\quad\text{C—N}^{\text{H}} & \text{HOC}\quad\text{C—N} \\
\quad|\qquad\|\qquad\diagdown\text{C=O} & \rightleftarrows\qquad\|\qquad\|\qquad\diagdown\text{COH} \\
\text{HN—C—N}_{\text{H}}^{\diagup} & \text{N—C—N}_{\text{H}}^{\diagup}
\end{array}
$$
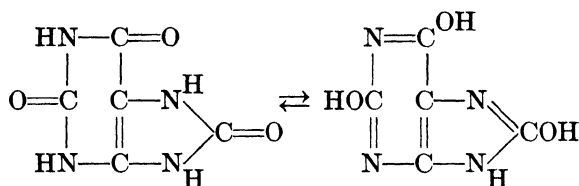
and it owes its weak acid powers to the hydrogens in the $\overline{}$COH groups of the enolic form. From the formula it may be seen that it is theoretically possible to replace three H atoms by metals. If the metal can shift to the N as does the H in forming the keto form, there is the possibility of the fourth H being replaced by metal, i.e.

$$
\begin{array}{lll}
\text{N=CONa} & \text{N=CONa} & \\
\quad|\qquad| & \quad|\qquad| & \\
\text{NaOC}\quad\text{C—N} & \text{NaOC}\quad\text{C—N}^{\text{Na}} & \\
\quad\|\qquad\|\qquad\diagdown\text{CONa}\quad\rightleftarrows & \quad\|\qquad\|\qquad\diagdown\text{CO}\quad\rightleftarrows & \\
\text{N—C—N}_{\text{H}}^{\diagup} & \text{N—C—N}_{\text{H}}^{\diagup} &
\end{array}
$$

$$
\begin{array}{ll}
\text{N=CONa} & \text{N=C}^{\diagup\text{ONa}} \\
\quad|\qquad| & \quad|\qquad| \\
\text{NaOC}\quad\text{C—N}^{\text{Na}} & \text{NaOC}\quad\text{C—N}^{\text{Na}} \\
\quad\|\qquad\|\qquad\diagdown\text{COH}\quad\rightleftarrows & \quad\|\qquad\|\qquad\diagdown\text{CONa} \\
\text{N—C—N}^{\diagup} & \text{N—C—N}^{\diagup}
\end{array}
$$
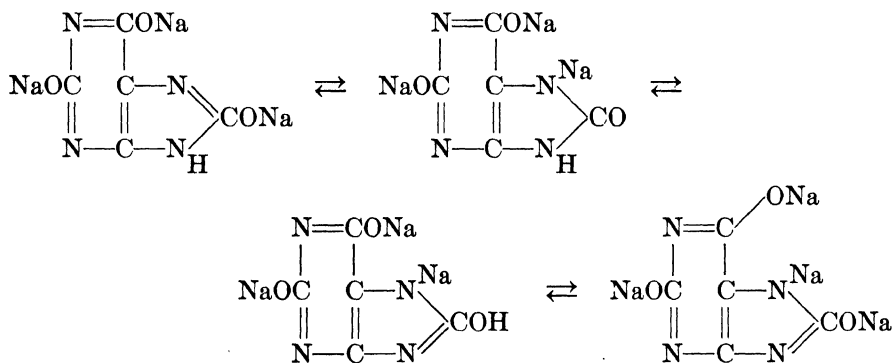
If this is so, four flats may be obtained. Each may be separate, or if the alkali necessary to keep them from decomposing is practically the same, two or more may be along the same level. Uric acid is, however, generally known as a weak dibasic acid. The enolization of two groups may suppress further enolization.

The work done on uric acid was at first similar to that on succinic acid, and the same difficulty of obtaining equilibrium was encountered. The various runs on uric acid are summarized in Table III. In absolute alcohol (Runs 1–3), no compound formation was obtained although mono-sodium urate is a

TABLE III

Summary of the Runs on Uric Acid

No.	Substance treated	Base used	Solvent	Time of run	Special treatment*	Result
1.	Uric acid	sodium isobuty-late	Absolute isobutyl alcohol	4 days	W 1 day	Apparent adsorption—rough curve
2.	"	NaOH	"	3 days	W 2 days	Apparent adsorption
3.	"	"	"	2 days	R 10½ hours	Scattered points approaching a flat to 2 equivalents
4.	"	"	99% isobutyl alcohol	"	"	Flat to 2 equivalents, then adsorption
5.	"	"	95% isobutyl alcohol	2 days	W 2 days	Flat to 2 equivalents, and a flat for the 3rd and
6, 7, 8.	"	"	"	3 days	W 2 days	one for the 4th equivalent
9.	Mono Na urate	"	Absolute isobutyl alcohol	3 days	W 3 days	Flat to 2 equivalents, then complete adsorption to 2.4 equiva-
10.	"	"	"	4 days	W 2 days	lents, and some
11.	"	"	"	5 days	W 2½days	little further adsorption
12.	Uric acid	"	95% ethyl alcohol	18 days	S 50 hrs.	Flat up to 1.1 equivalents, then apparent adsorption
13.	"	"	"	6¼ days	W 5½ days S occasionally	Flat up to nearly 2 equivalents, then apparent adsorption
14.	"	"	"	37 days	W 35 days	Flat to 2 equivalents, then very little adsorption

* W = warm (at 50°-60° on top of an oven).
  R = refluxed.
  S = shaken in a mechanical shaker. See p. 1303.

definite and well-known compound. With the addition of a small amount of water (Runs 4–8), compound formation occurred. The question immediately came up as to whether there were true adsorption or a lack of equilibrium conditions in the anhydrous medium. The third run by approaching a flat, favors the latter view, although it may be argued that under the vigorous conditions of the experiment, any small amount of water in the alcohol (which was not specially treated) could be utilized. In order to test experimentally between adsorption and compound formation without equilibrium, further runs were made. If any curve represents equilibrium conditions it should be possible to reach it from either side. In this case mono-sodium urate put into absolute isobutyl alcohol containing less than equilibrium amounts of NaOH, should give up NaOH until equilibrium is reached. Accordingly mono-sodium urate was made. (This was done by adding the requisite amount of uric acid, evaporating to dryness, and air drying. It was acid to phenol-phthalein, showing the absence of free NaOH, and alkaline to methyl red.) Runs 9–11 show that instead of reaching the apparent adsorption curve, there was still further compound formation.

However, Beilstein and Meyer and Jacobson[1] state that mono-sodium urate contains one molecule of water of crystallization. Certain compounds are known to exist only with molecules of solvation, as for example $KI_3 \cdot H_2O$ and $KI_7 \cdot H_2O$.[2] If the mono-sodium urate could not exist without this molecule of water, we would have a very logical explanation for adsorption in absolute alcohol and compound formation in alcohol containing water. When moisture determinations were run on the salt, which had been made in the usual way (drying at 110° and then evacuating to about 11 mm. of mercury) less than three percent of moisture was obtained. One molecule of water of crystallization would correspond to 9.47%. By heating to 140°–150° for three weeks, about 5% of moisture was driven off (or the compound may have slowly volatilized). Determination of the nitrogen by the Kjeldahl method was finally resorted to as the simplest and most accurate method. It gave a moisture content of 11.62%, and showed that if the salt could exist without water of crystallization, the water was at least very firmly bound. As a final test of this point, nearly anhydrous mono-sodium urate was put into absolute isobutyl alcohol. (Mono-sodium urate containing only 0.5% moisture was prepared by heating the moisture-containing salt to 140°–150° in an oil bath while simultaneously evacuating to less than 10 mm. of mercury for a period of about 15 hours.) The anhydrous salt lost no free NaOH in 15 days as indicated by neutrality of the supernatant liquid to phenolphthalein. It is, therefore, possible for the mono-sodium urate to exist in absolute isobutyl alcohol without water of crystallization. Equilibrium in the anhydrous alcohol is reached very slowly, and adsorption is simulated. This is an important warning.

After the formation of the mono-sodium salt, the formation of the di-sodium salt occurs with relative ease. In 95% isobutyl alcohol (Runs 5–8), there is then clear indication of the formation of the tri- and tetra-sodium

[1] "Lehrbuch der organischen Chemie," 2 III, 1307 (1920).
[2] Grace: J. Chem. Soc., 1931, 594.

TABLE IV

Uric Acid and NaOH in 95% Isobutyl Alcohol

1 gm. uric acid, which requires 5.95 cc. of N NaOH to form the mono-sodium salt, used for each number

Length of run—3 days. Kept at 50°–60° for 2 days

No.	a. cc. N NaOH added	b. Total vol. of liquid added cc.	c. cc. N acid (or base) for 1 cc. sup. liq.	d. cc. N base in super. liquid $c \times b/10$	e. cc. N base used NaOH used $a - d$	f. Equiv. of NaOH used $e/5.95$
1.	0.00	20	0.01 base	0.00	0.00	0.00
2.	1.14	20	0.03 "	0.00	1.14	0.19
3.	2.28	20	0.04 "	0.00	2.28	0.39
4.	4.56	20	0.04 "	0.00	4.56	0.75
5.	5.70	20	0.05 "	0.00	5.70	0.97
6.	6.84	20	0.06 "	0.00	6.84	1.17
7.	9.13	20	0.00 "	0.00	9.13	1.54
8.	11.41	20	0.00 "	0.00	11.41	1.93
9.	13.69	20	0.01 acid	0.01	13.68	2.31
10.	15.17	20	0.15 "	0.29	14.88	2.50
11.	16.25	20	0.17 "	0.33	15.92	2.68
12.	17.33	20	0.15 "	0.29	17.04	2.86
13.	18.42	20	0.17 "	0.33	18.09	3.04
14.	20.58	20	0.25 "	0.51	20.08	3.37
15.	3.61	20	0.01 base	0.00	3.61	0.61
16.	8.50	20	0.00 "	0.00	8.50	1.43
17.	10.61	20	0.01 acid	0.01	10.60	1.78
18.	12.63	20	0.04 "	0.09	12.54	2.11
19.	17.13	20	0.21 "	0.42	16.72	2.81
20.	19.39	30	0.18 "	0.54	18.85	3.17
21.	21.24	30	0.26 "	0.77	20.48	3.44
22.	23.00	30	0.40 "	1.21	21.78	3.66
23.	2.18	20	0.10 base	0.00	2.18	0.37
24.	3.82	20	0.11 "	0.00	3.82	0.64
25.	6.00	20	0.01 "	0.00	6.00	1.01
26.	11.99	30	0.01 acid	0.04	11.96	2.01
27.	13.09	30	0.03 "	0.08	13.01	2.19
28.	14.18	30	0.05 "	0.16	14.01	2.36
29.	19.27	30	0.19 "	0.58	18.69	3.14
30.	23.00	30	0.30 "	0.90	22.09	3.71
31.	23.90	40	0.26 "	1.03	22.87	3.84
32.	25.97	40	0.30 "	1.20	24.77	4.16

salts. (See Table IV and Fig. 2) Each flat is extended somewhat beyond its theoretical limit by adsorption of alkali on it. The amount of alkali in equilibrium with each of them is nearly the same. In 95% ethyl alcohol (Runs 12-14), the formation of the di-sodium salt is very much slower than it is in 95% isobutyl alcohol. Run 14 (Table V and Fig. 2), showing only apparent adsorption on the di-sodium salt, would certainly have been taken as the equilibrium curve if the work in isobutyl alcohol had not been done first. But if the tri- and tetra-sodium salts are formed in one case, they must be in the other, unless we make the assumption that they exist only with molecules of one of the solvents as part of the compound. Uric acid was treated in isobutyl alcohol with NaOH, so as to contain about three equivalents of alkali. This was put into 95% ethyl alcohol containing such an amount of NaOH that it was less than that required by the curve for Run 14, and too much for that required by the curves from Runs 8-11. After standing at about 40° for three weeks, no change was appreciable in the composition of either the solid or liquid phases. But after refluxing for 22 ½ hours, the composition of the solid and liquid approached closely a point on the curve for isobutyl alcohol.

TABLE V

Uric Acid and NaOH in 95% Ethyl Alcohol

1 gm. uric acid, which requires 5.95 cc. of N NaOH to form the mono-sodium salt, used for each number

Length of run—37 days   Kept at 40°–60° for 35 days

Total volume at liquid added—25 cc.

No.	a cc. N NaOH added	b cc. N acid (or base) for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2.5	d cc. N base used a − c	e Equiv. of NaOH used d/5.95
1.	1.15	0.03 base	0.00	1.15	0.19
2.	3.45	0.03 "	0.00	3.45	0.58
3.	5.75	0.02 "	0.00	5.75	0.97
4.	6.90	0.01 "	0.00	6.90	1.16
5.	9.20	0.01 "	0.00	9.20	1.55
6.	10.35	0.00 "	0.00	10.35	1.74
7.	12.65	0.02 acid	0.04	12.61	2.12
8.	14.95	0.62 "	1.54	13.41	2.25
9.	16.10	0.50 "	1.25	14.85	2.50
10.	18.40	1.80 "	4.51	13.90	2.34
11.	19.55	2.22 "	5.54	14.01	2.35
12.	21.85	2.95 "	7.27	14.48	2.43
13.	23.00	2.97 "	7.42	15.58	2.62
14.	25.30	3.96 "	9.91	15.39	2.59
15.	26.45	4.57 "	11.43	15.02	2.52
16.	28.75	5.31 "	13.80	14.95	2.51

This gave a strong confirmation of the correctness of that curve and of the formation of the tri- and tetra-sodium salts. Equilibrium in 95% ethyl alcohol is reached very slowly indeed in the last part of the curve.
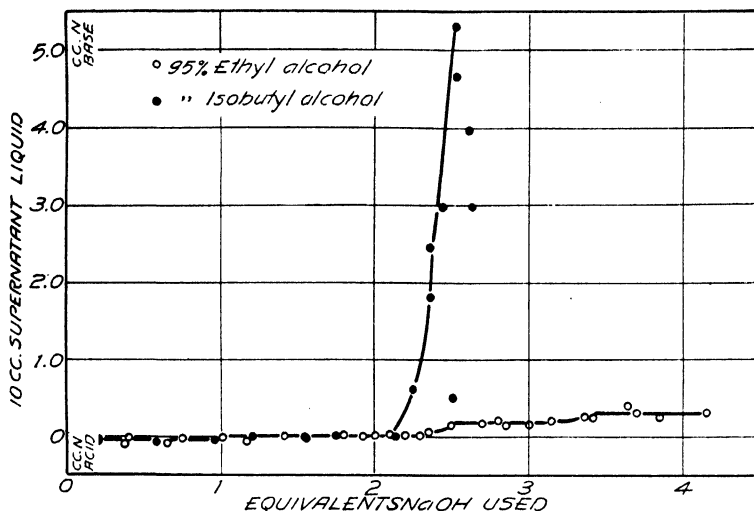
FIG. 2

Uric Acid and NaOH

3. *Uracil.*

Uracil has the formula

$$\begin{array}{ccc} & H & O \\ N\!\!-\!\!C\!\!-\!\!N & H \\ | & & | \\ C\!\!=\!\!C\!\!-\!\!C\!\!=\!\!O \\ H & H \end{array}$$
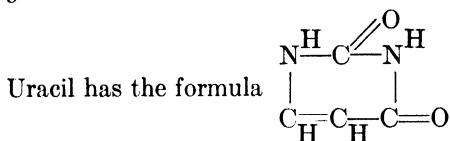
which shows its relation to uric acid. According to Levene and Bass,[1] it is a mono-basic acid. Either of the keto groups in the above formula may enolize to give the acidic properties, but enolization of one group inhibits that of the other. They say it does not react with acids. If the formula given above is the only one considered, it should not react with acids according to the criteria set forth by Bancroft and Barnett.[2] However they found that it did react with gaseous HCl at 20 mm. pressure.[3] They give four alternative formulae, each obtained by a shift of one hydrogen, which would account for this reaction.

When we treated uracil with NaOH in 95% ethyl alcohol, it formed the sodium salt quite readily. The salt was a voluminous precipitate and tended to cake, but alternate shaking and heating to 50°–60° obviated this difficulty and quickened the speed of the reaction. Data are given in Table VI and Fig. 3. With HCl there was no compound formation and very little adsorption even after three days of refluxing.

[1] "Nucleic Acids" (1931).

[2] J. Phys. Chem., **34**, 753 (1930).

[3] J. Phys. Chem., **34**, 1244 (1930).
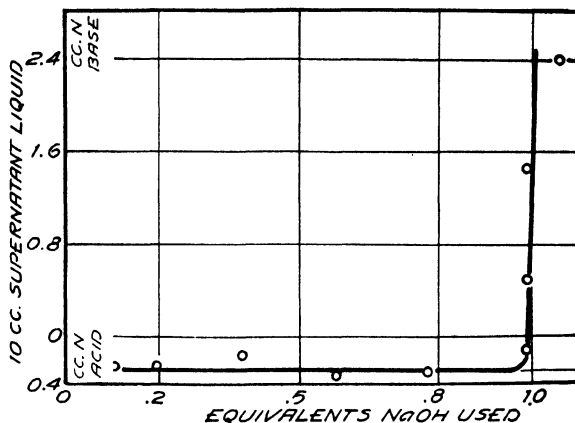
FIG. 3
Uracil and NaOH in 95% Ethyl Alcohol

TABLE VI

Uracil and NaOH in 95% Ethyl Alcohol

0.5602 gm. uracil, which theoretically reacts with 5 cc. N NaOH, used for each number

Volume in each number—20 cc.

Kept at 50°–60° for 4 days
Shaken occasionally

No.	a cc. N NaOH added	b cc. N acid (or base) for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2	d cc. N base used a − c	e Equiv. of NaOH used d/5
1.	0.56	0.26 base	0.00	0.56	0.11
2.	1.01	0.26 "	0.00	1.01	0.20
3.	1.91	0.16 "	0.00	1.91	0.38
4.	2.91	0.33 "	0.00	2.91	0.58
5.	3.92	0.30 "	0.00	3.92	0.78
6.	4.93	0.10 "	0.00	4.93	0.99
7.	5.94	0.50 acid	0.99	4.95	0.99
8.	7.84	1.46 "	2.91	4.93	0.99
9.	10.09	2.39 "	4.78	5.31	1.06

3. *Alanine*—Alanine was chosen as typical of amino acids which would show a behavior more similar to the proteins than any simpler substances. It is insoluble in alcohol. When NaOH in 95% ethyl alcohol was added to the alanine, there was some peptization which became more apparent as the strength of the alkali increased and became complete when one equivalent or more of base had been added. The peptization of the product seemed to render the method useless for alanine, and to make it of doubtful value for proteins. Efforts were made to save the method. Various solvents such as

ether, benzene, carbon tetrachloride, and isobutyl alcohol were added in an unsuccessful attempt to precipitate the sodium salt of the alanine which was known to be present. Several tests were made which convinced us that the sodium salt was peptized rather than in true solution. For instance the sodium salt of the alanine, which was made in the same way as those of succinic and uric acids, was insoluble in alcohol. The sodium salt, put into apparent solution in alcohol by NaOH, was dialyzed against alcohol, and practically nothing went through the membrane. Then it was found that solid sodium alaninate did not interfere with the titration of NaOH by acid in alcoholic solution, using phenolphthalein as indicator. Since the peptized sodium alaninate is simply finely divided solid, it should not interfere with the titra-
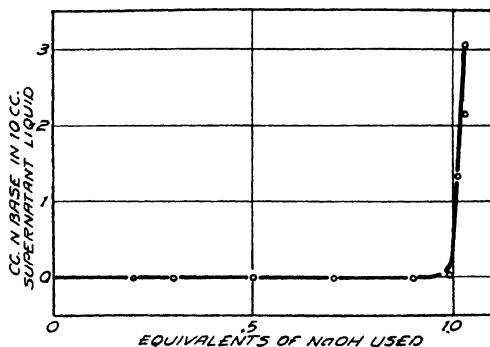
FIG. 4

Alanine and NaOH in 95% Ethyl Alcohol

TABLE VII

Alanine and NaOH in 95% Ethyl Alcohol

0.8906 gm. alanine, which theoretically reacts with 10 cc. N NaOH, used for each number

Total volume of liquid added was 22 cc. in each case

Length of run—3 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2.2	d cc. N base used a − c	e Equiv. of NaOH used d/10
1.	2.00	0.00	0.00	2.00	0.20
2.	3.00	0.00	0.00	3.00	0.30
3.	5.00	0.00	0.00	5.00	0.50
4.	7.00	0.00	0.00	7.00	0.70
5.	9.00	0.00	0.00	9.00	0.90
6.	10.00	0.05	0.11	9.89	0.99
7.	13.00	1.34	2.94	10.06	1.01
8.	15.00	2.14	4.71	10.29	1.03
9.	17.00	3.05	6.71	10.29	1.03

tion of unused NaOH by acid. It was found to behave in the expected manner, and the method was therefore applicable if the supernatant liquid were titrated in alcoholic solution. The titration was found to be more satisfactory when thymolphthalein was used as indicator. The data in Table VII and the curve in Fig. 4 show the result of this modification of the method.

When alanine was treated with HCl in 95% ethyl alcohol, peptization occurred in the same way as with the NaOH. A very similar method was used
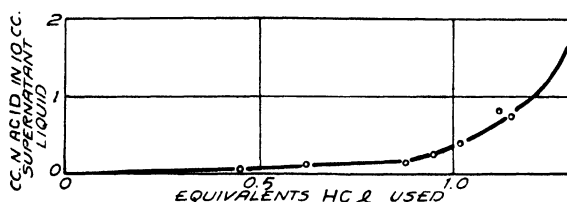
FIG. 5
Alanine and HCl in 95% Ethyl Alcohol

to titrate the excess acid in the supernatant liquid. It was done in alcoholic solution using the acid change of thymol blue as indicator. The results are not as gratifying as those with NaOH and thymolphthalein, and the curve leaves some doubt of compound formation; but the break in the curve occurs at just about the theoretical point. This is shown in Table VIII and Fig. 5.

If a suspension of finely powdered alanine in alcohol is used, alcoholic base may be added directly and a direct titration of the amino acid with alkali may be made, using thymolphthalein as indicator. There must be constant shaking and a permanent blue must be reached. The titration takes from 20

TABLE VIII

Alanine and HCl in 95% Ethyl Alcohol

0.8906 gm. alanine, which theoretically reacts with 10 cc. N HCl, used for each number

Total volume of liquid added was 20 cc. in each case, except 7 which was 30 cc. Length of run—4 days

No.	a cc. N HCl added	b cc. N base for 10 cc. sup. liq.	c cc. N acid in super. liquid b × 2	d cc. N acid used a − c	e Equiv. of HCl used d/10
1.	4.57	0.06	0.12	4.45	0.45
2.	6.39	0.12	0.23	6.16	0.62
3.	9.13	0.15	0.31	8.82	0.88
4.	10.04	0.25	0.50	9.54	0.95
5.	10.96	0.39	0.77	10.19	1.02
6.	12.78	0.81	1.61	11.17	1.12
7.	13.70	0.73	2.18	11.52	1.15
8.	16.43	1.72	3.45	12.99	1.30

to 30 minutes for a gram of alanine. This is similar to the alcoholic titration worked out by Foreman,[1] Willstätter and Waldschmidt-Leitz,[2] and Harris;[3] and which has been used by many others[4] in its original or a modified form. This titration was not known to us until after the work on alanine had been done. It seems to have been overlooked by many others besides ourselves, although it appears to be a common and useful tool among biochemists. We have found it indispensable.

It depends on the fact that in alcoholic solution, most weak acids, bases, and ampholytes are neutral to the rather high or low pH change of the indicators used. Salts, as they are formed during titration with strong acid or base, do not hydrolyze and therefore do not react with the indicator. After the end-point has been reached, any excess strong acid or base added will affect the indicator. If an appreciable amount of the acid or base is needed to bring a volume of alcohol equal to that in the titration flask to the end-point of the indicator, that amount must be subtracted as a blank from the results obtained. The use of this method of titration obviously limits us to the reactions of strong acids and bases with the substances we wish to examine.

The facts of the alcoholic titration are quite adequately and easily described in the foregoing paragraph, but the theory is not so readily explained. This is partly because experimental work supporting a theory of acidimetry depends on accurate measurements of hydrogen ion concentration. These are difficult to make in non-aqueous solutions and still involve certain assumptions which probably introduce errors. It is generally agreed, however, that the degree of dissociation is less in alcohol and most other non-aqueous solvents than in water, for it depends on the dielectric constant of the solvent. Walden[5] finds as an approximation that $D_1:D_2 = \sqrt[3]{v_1} : \sqrt[3]{v_2}$, where D_1 and D_2 are the dielectric constants of the solvents and v_1 and v_2 are the dilutions of a strong electrolyte when the amount of dissociation is equal. Dissociation constants have been determined conductometrically in alcohol by Hartwig[6] for formic, acetic and butyric acids, and by Goldschmidt[7] and his co-workers for quite a number of organic acids and bases. Constants were determined potentiometrically in alcohol by Michaelis and Mizutani[8] for acetic, propionic, lactic, salicylic, benzoic, phosphoric and carbonic acids, ammonia, glycine, and amino-benzoic acid. They are lower than in water.

Then an acid is weaker in alcohol than in water, and if other conditions are the same, it should have a smaller range of pH at the point where an

[1] Biochem. J., 14, 451 (1920).

[2] Ber., 54B, 2988 (1921); Z. physiol. Chem. 161, 191 (1926).

[3] Proc. Roy. Soc., 95B, 440, 500 (1923); 97B, 364 (1925); 104B, 412 (1929).

[4] Schidrowitz: Analyst, 28, 233 (1903); Sutton: "Volumetric Analysis," 8th edit. p. 38 (1900), (This is the reference which gave Foreman his clue); Vorländer: Ann., 341, 73, 75 (1905); Ber., 52B, 309 (1919); Birckner: J. Biol. Chem., 38, 245 (1919); Woodman: J. Agri. Science, 12, 231 (1922); Bishop, Kittridge, and Hildebrand: J. Am. Chem. Soc., 44, 135 (1922); Martens: Bull. Soc. chim. biol., 9, 454 (1927).

[5] Z. physik. Chem., 54, 228 (1905); 94, 263 (1920).

[6] Wied. Ann., 33, 58 (1888); 43, 838 (1891).

[7] Z. physik. Chem., 89, 129 (1914); 91, 46 (1916); 99, 116 (1921).

[8] Z. physik. Chem., 116, 135 (1925).

equivalent amount of base has been added and should accordingly have a less distinct end-point. But there is very little alcoholysis (corresponding to hydrolysis) so the break in the titration curve at the equivalent point is very much sharper and the end-point is also much sharper. The amount of alcoholysis is low, for although the dissociation of the acid is less, that of the alcohol is very much less than that of water.[1] If the salt formed is soluble in the alcohol, the pH at which the break or vertical portion of the titration curve commences will be relatively high due to the depressing effect of the salt on the ionization of the acid. If the salt is absolutely insoluble, the vertical portion of the titration curve can not start above the pH of the neutral solvent; for only acid will be present until it is all used up, and by definition acid dissociates to give hydrogen ions. Then the titration curve of all acids forming insoluble salts with a given base will be the same above the pH of the neutral solvent. This of course is a limiting case and is never actually realized. It would however tend to lower the pH of an end-point. Similar reasoning applies to weak bases.

We have left out of our discussion the effect of the alcohol on the pH range of the indicator, for we do not know accurately what it is. Hildebrand[1] has shown that the relative pH ranges are the same for the majority of indicators, but that some are shifted (i.e. cyanine is more acid in alcohol).

Experimentally, we find these facts. Very weak acids, such as the phenols and certain inorganic acids—boric, hydrocyanic, etc.—can not be titrated in water solution. Neither can they be titrated in alcoholic solution, but a larger proportion of the equivalent alkali may be added before the indicator is affected. In the case of boric acid with thymolphthalein in alcohol, the end-point is quite good, so that probably a given percentage could be titrated consistently. The carboxylic acids with the exception of the amino acids, may be titrated satisfactorily in water with phenolphthalein. In alcohol, though the dissociation constants are less, and they are consequently weaker, they can still be titrated with phenolphthalein. Sodium carbonate, which is the salt of an acid of strength intermediate between the carboxylic acids and the phenols, is acid to thymolphthalein in alcohol. It gives phenolphthalein a faint pink color. It is strongly alkaline to both these indicators in water.

When we come to apply this reasoning to amino acids, we may assume, as has been done until recently, that they dissociate either as a weak acid or base to give hydrogen or hydroxyl ions, according to the equations:

$$H_2N-R-COOH \rightleftarrows H_2N-R-COO^- + H^+$$

$$H_2N-R-COOH + H_2O \rightleftarrows {}^+H_3N-R-COOH + OH^-.$$
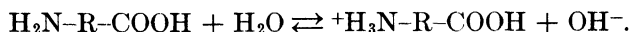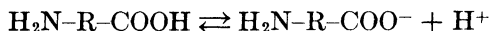
Adding alcohol would make the end-point sharper for the reasons given above. Or we may follow Bjerrum's[2] generally adopted "zwitterion" theory according to which the amino acid is present in neutral solution to a greater or lesser extent as an internal salt, $^+H_3N-R-COO^-$. When NaOH is added, the Na$^+$

[1] Cf. Hildebrand: J. Am. Chem. Soc., 44, 135 (1922).

[2] Z. physik. Chem., 104, 147 (1923).

replaces the $- NH_3^+$ of the "zwitterion" to form $^+H_3N-R-COONa$; and when HCl is added, the Cl^- replaces $- COO^-$ to form $ClH_3N-R-COO^-$. In either case we are titrating a weak acid or base made still weaker by a substituted group of opposing tendency, and in either case titration will be made more satisfactory in alcohol. It is not necessary, then, to assume the "zwitterion" hypothesis.

Proteins

The general method was applied to the proteins just as outlined in the introduction. The work on alanine had led us to believe that there might be some peptization of the protein in acid or alkaline solution. With some pro-
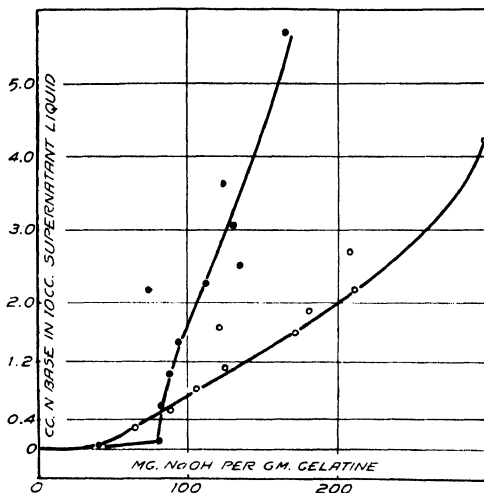
FIG. 6
● Titration in water
○ Titration in alcohol

teins, this was practically complete, and with some it was negligible. A good idea of its amount could be obtained by titrating the $-COOH$ or $-NH_2$ groups in the supernatant liquid (by finding the amount of acid necessary to change the reaction from just blue to thymolphthalein to just red to thymol blue or vice versa).[1] However, the titrations were made directly on the undiluted supernatant liquid with acid or alkali in 95% ethyl alcohol in the same way as they were done for alanine. Consequently, we titrated only excess strong acid or base, and not any peptized protein, protein salt, adsorption complex, or any possible hydrolysis products or their salts. The results of using water solution for the titration of a peptized protein are shown graphically in Fig. 6, where they are compared with results of titration in alcohol. The endpoints in the water solution were very indistinct.

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[1] Cf. Harris: Proc. Roy. Soc., **95B**, 500 (1923).

Robertson[1] and Hoffman and Gortner[2] make some objections to the use of indicators in determining the amount of acid or base bound by a protein, especially when it is in apparent solution. We feel that the alcoholic titration outlined meets most of these. The end-points are quite good in alcohol, especially with thymolphthalein. A second objection is that in colorimetric titrations, only the amount of acid or base bound at the particular pH of the indicator change is determined. In the alcoholic solution, the pH of all proteins and practically all of their possible products, is within the pH ranges of the indicators used. After equilibrium has been reached under any desired conditions, free acid or base *only* is titrated. The removal of the acid or base in most cases disturbs the equilibrium, and the system immediately starts to re-establish it. In alcohol, especially with proteins, we have found that this is a slow process, so that there would be no appreciable change in the one or two minutes required for titration. The third objection, that the indicators may change the protein, holds except when it is disproven in specific instances. We are confident that our indicators were perfectly satisfactory in this respect.

Equilibrium was slow with succinic and uric acids, and the work on uric acid showed that lack of equilibrium may appear to be adsorption. Consequently a time which may seem inordinately long was given for the proteins to reach equilibrium. Less time was allowed when peptization occurred as there could then be more intimate contact. Shaking was also employed to bring about equilibrium by keeping the solid and liquid phases thoroughly mixed. The shaking apparatus consisted of a large platform having places for 100 bottles, suspended from a frame by pliable iron strips. The platform was given a back and forth motion by an eccentric run by a motor. There were about 150 complete shakes a minute.

The long time of the runs made hydrolysis of the proteins seem quite probable, although the presence of alcohol was a factor opposing it. It was tested for in the following manner. The supernatant liquid of the number in each run which contained the largest amount of acid or base was titrated as usual. The liquid in the titration flask was returned quantitatively to the bottle. Sufficient further acid or base was then added to neutralize all the base or acid originally used. The bottle now contained salt and the original protein or its hydrolysis products in alcohol. The alcohol was pumped off. The material left was analyzed for amino nitrogen by the method of Van Slyke and Birchard.[3] A gram of the original protein was subjected to an identical analysis. The amino nitrogen content of the completely hydrolyzed protein was taken from the literature or calculated. It is obvious from its use in the following equation that it does not need to be very exact. Then if a is the percent of nitrogen as amino nitrogen in the original protein, b that of the material used in the run, and c that of the completely hydrolyzed material; $(b - a)/(c - a)$ is the fraction of hydrolysis which has taken place. These values are a maximum, for any error in the method would be due to further

[1] "The Physical Chemistry of the Proteins" (1918).

[2] Colloid Symp. Mon., **2**, 209 (1925).

[3] J. Biol. Chem., **16**, 539 (1913-14).

hydrolysis in its execution. With acids, the hydrolysis was uniformly low (not more than 2.5%) with the exception of that of zein in 85% acetone. In alkali, the hydrolysis of all the proteins except casein was much higher. It ranged from 10% to 40%. This method of determining hydrolysis is open to the objection that the increase in amino groups may not always parallel the amount of hydrolysis, but it is sufficiently accurate for our purpose.

Moisture determinations on the proteins were made by heating them to about 60° in a desiccator which was at the same time evacuated to low pressure. This treatment was carried out for about 25 hours. The results are given below, as the percent of the original weight which was lost in heating.

Casein	9.9%
Gelatine	11.4
Zein	3.7
Gliadin	5.5
Edestin	7.2

All data given for proteins has been calculated on the dry basis.

TABLE IX

Summary of the Runs on Proteins

No.	Protein	Source	Reacts with	Solvent	Length of run	Time of shaking
1.	Casein	Kahlbaum	HCl	95% ethyl alcohol	52 days	343 hrs.
2.	Casein	,,	NaOH	,,	,,	317 hrs.
3.	Gelatine	Eastman	HCl	,,	53 days	285 hrs.
4.	Gelatine	,,	,,	,,	30 days	290 hrs.
5.	Gelatine	,,	,,	Absolute alcohol	48 days	385 hrs.
6.	Gelatine	,,	NaOH	95% ethyl alcohol	14 days	— —
7.	Gelatine	,,	,,	,,	,,	— —
8.	Gelatine	,,	,,	,,	25 days	270 hrs.
9.	Gelatine	,,	,,	,, with 52% benzene	53 days	285 hrs.
10.	Zein	Conn. Agr. Expt. Sta.	HCl	95% ethyl alcohol	21 days	190 hrs.
11.	Zein	,,	NaOH	,,	35 days	350 hrs.
12.	Zein	,,	HCl	85% acetone	35 days	450 hrs.
13.	Zein	,,	NaOH	,,	,,	,,
14.	Gliadin	Univ. of Minnesota	HCl	95% ethyl alcohol	30 days	345 hrs.
15.	Gliadin	,,	NaOH	,,	,,	,,
16.	Edestin	Eimer and Amend	HCl	,,	31 days	330 hrs.
17.	Edestin	,,	NaOH	,,	,,	,,

TABLE IX

Summary of the Runs on Proteins

No.	Amount of peptization	App. amt. of hydrolysis	Compound formation	Mg. per gm. protein	Equiv. $\times 10^{-5}$	Combining weight
1.	None	0.8-0.9%	+	61	167	600
2.	Negligible	0.7%	+	75	187	535
3.	Considerable in high nos.	2.5%				
4.	"	"	+	25	68	1470
				might be considered to be		
5.	None	2.3%		31	86	1160
6.	Complete	40%				
7.	"	"	+	30	75	1330
8.	Some	17-18%				
9.	Considerable	37%	?	—	—	• —
10.	Considerable	2%	—	—	—	—
11.	Complete	27%	+	28	70	1430
12.	Considerable	15%	—	—	—	—
13.	Considerable	20%	?	—	—	—
14.	None	1.4%	—	—	—	—
15.	Some	14%	+	25	62	1613
16.	Negligible	1.4%	+	45	124	806
17.	Negligible	11%	+	43	108	925

It will be well, before taking up the specific proteins, to consider briefly some of the difficulties encountered in interpreting the curves obtained. Theoretically there are none, but practically they are met. There is first the possibility of such complete adsorption that the amount of substance left in the supernatant liquid is too small to be detected experimentally. The curve then appears to show compound formation. Examples of this are the adsorption of dyes by charcoal, and some of our own work on succinic acid. Then a lack of equilibrium in compound formation, due to its slowness, may appear as an adsorption curve. This situation was met several times during the experiments on uric acid. Hydrolysis of the protein must profoundly affect the shape of the curve. In the proteins used, there is roughly from 15 to 70 times as much amino nitrogen in the completely hydrolyzed as in the unhydrolyzed material; so that even one per cent hydrolysis would mean at least a fifteen per cent increase in the amount of amino nitrogen. This makes the protein in the higher numbers of each run, where there is most hydrolysis, appear to take up more acid or especially more alkali, than is really the case. In the lower numbers of each run, particularly in acid, this is cut down to negligible proportions. Fortunately for us, it is these lower numbers which determine whether or not a compound is formed. The amount of adsorption on the original protein or on any compound formed, as determined from the upper part of the curve, is unreliable.

We do not claim that our results will be applicable to water solution. Too often results have been compared which have been obtained under radically different experimental conditions. It would take a vast amount of work to harmonize them. Our results are simply those under the conditions of our experiments. Some agree well with values obtained in water solution. We will give the results of other workers for the different proteins. Many times, they give the maximum amount bound, while we give that present in the compound.

In order to facilitate comparisons between the different proteins, all the results on them are given in Table IX.

FIG. 7

Casein and HCl in 95% Ethyl Alcohol

1. *Casein*—The casein was a technical product purchased from Kahlbaum and used without further purification. The runs in both acid and alkali seemed perfectly normal in every way. In acid, the appearance of the casein did not change during the run. In alkali, it became somewhat yellow and swollen, but there was apparently no peptization. The hydrolysis of the casein in each case was less than one percent.

Casein formed a hydrochloride (Table X and Fig. 7), as Bancroft and Barnett[1] found, and there was then adsorption to a slight extent on the compound. It contained 61 mg. HCl per gm. of casein or 167×10^{-5} equivalents. This gives casein a combining weight with the acid of about 600. Bancroft and Barnett's compound contained 234×10^{-5} equivalents. Other results reported are:

90×10^{-5} equivalents at a pH of 2.5 and 600×10^{-5} equivalents at the maximum acid concentration by Hoffman and Gortner[2]

85×10^{-5} equivalents at a pH of 2.5 by Sandstrom[3]

33×10^{-5} equivalents when acid is "saturated" with protein by Robertson[4]

60×10^{-5} equivalents at neutrality to phenolphthalein by Bracewell[5]

59×10^{-5} equivalents by Hitchcock[6]

72×10^{-5} equivalents by Loeb[7] as recalculated by Cohn.[8]

[1] J. Phys. Chem., **34**, 449 (1930).
[2] Colloid Symp. Mon., **2**, 209 (1925).
[3] J. Phys. Chem., **34**, 1071 (1930).
[4] J. Phys. Chem., **13**, 469 (1909).
[5] J. Am. Chem. Soc., **41**, 1511 (1919).
[6] J. Gen. Physiol., **5**, 383 (1922-1923).
[7] J. Gen. Physiol. **3**, 547 (1920-1921).
[8] Physiol. Rev., **5**, 349 (1925).

TABLE X

Casein and HCl in 95% Ethyl Alcohol

1 gm. casein, equivalent to .901 gm. dry casein, used in each number

Volume of each number—20 cc.   Length of run—52 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm.casein equiv. × 10^{-3} (a − c)/.901	e mg. HCl per gm. casein d × 36.46
1.	0.50	0.00	0.00	0.56	20.5
2.	1.01	0.00	0.00	1.13	41.0
3.	1.52	0.01	0.01	1.67	61.0
4.	2.03	0.25	0.51	1.69	61.5
5.	2.54	0.38	0.76	1.97	71.7
6.	4.05	1.05	2.09	2.18	79.3
7.	4.56	1.30	2.60	2.18	79.4
8.	5.07	1.50	3.01	2.29	83.5

TABLE XI

Casein and NaOH in 95% Ethyl Alcohol

1 gm. casein, equivalent to .901 gm. dry casein, used in each number

Volume of each number—20 cc.   Length of run—52 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. casein equiv. × 10^{-3} (a − c)/.901	e mg. NaOH per gm. casein d × 40.008
1.	0.50	0.00	0.00	0.56	22.2
2.	1.00	0.00	0.00	1.11	44.4
3.	1.50	0.00	0.00	1.66	66.6
4.	2.00	0.00	0.01	2.21	88.4
5.	2.50	0.01	0.01	2.76	110.4
6.	3.00	0.05	0.10	3.21	128.6
7.	3.50	0.23	0.46	3.37	134.9
8.	4.00	0.19	0.38	4.02	160.9
9.	4.50	0.38	0.75	4.16	166.3
10.	5.00	0.49	0.97	4.47	178.9
11.	10.00	2.02	4.05	6.62	264.7

Casein also formed a compound with NaOH (Table XI and Fig. 8) as was expected from its acidic character and much previous work done on it. There was considerable adsorption on this. It contained about 75 mg. NaOH per gm. casein or 187×10^{-5} equivalents, and gives casein a combining weight with strong base of 535. This is much more base than is contained
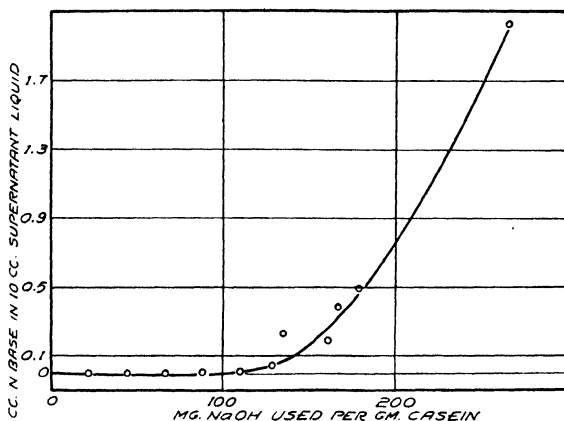
FIG. 8

Casein and NaOH in 95% Ethyl Alcohol

in the "caseinates" often mentioned. This result may be compared with others reported:

11×10^{-5} equivalents when base is "saturated" with protein by Robertson[1] and L. L. Van Slyke and Bosworth[2]

50-55 $\times 10^{-5}$ equivalents at neutrality to litmus by Robertson,[3] L. L. Van Slyke and Hart,[4] and Söldner[5]

90×10^{-5} equivalents at neutrality to phenolphthalein by L. L. Van Slyke and Hart,[4] Söldner,[5] Bosworth and L. L. VanSlyke,[6] Laqueur and Sackur,[7] and Courant[8]

11.2, 21.4, 58.4 and 87.2 $\times 10^{-5}$ equivalents in Mg. compounds of casein by L. L. Van Slyke and Winter[9]

90×10^{-5} equivalents at a pH of 10.2, 155×10^{-5} at a pH of 10.5, and a maximum of 1400×10^{-5} by Hoffman and Gortner[10]

[1] J. Phys. Chem., **13**, 469 (1909).

[2] J. Biol. Chem., **14**, 211 (1913).

[3] J. Phys. Chem., **14**, 528 (1910).

[4] Am. Chem. J., **33**, 461 (1905).

[5] Z. angew. Chem., **1895**, 370.

[6] J. Biol. Chem., **14**, 207 (1913).

[7] Beiträge Z. chem. Physiol., **3**, 193 (1902).

[8] Archiv ges. Physiol., **50**, 109 (1891).

[9] J. Biol. Chem., **17**, 287 (1914).

[10] Colloid Symp. Mon., **2**, 209 (1925).

146 × 10^{-5} equivalents at a pH of 10.5 by Sandstrom[1]

136-40 × 10^{-5} equivalents "under some conditions" by Cohn[2]

155-60 × 10^{-5} equivalents by Greenberg and Schmidt[3] and by Cohn and Berggren[4] if casein is not "nach Hammarsten"

180 × 10^{-5} equivalents by Robertson[5] and Cohn and Berggren[4]
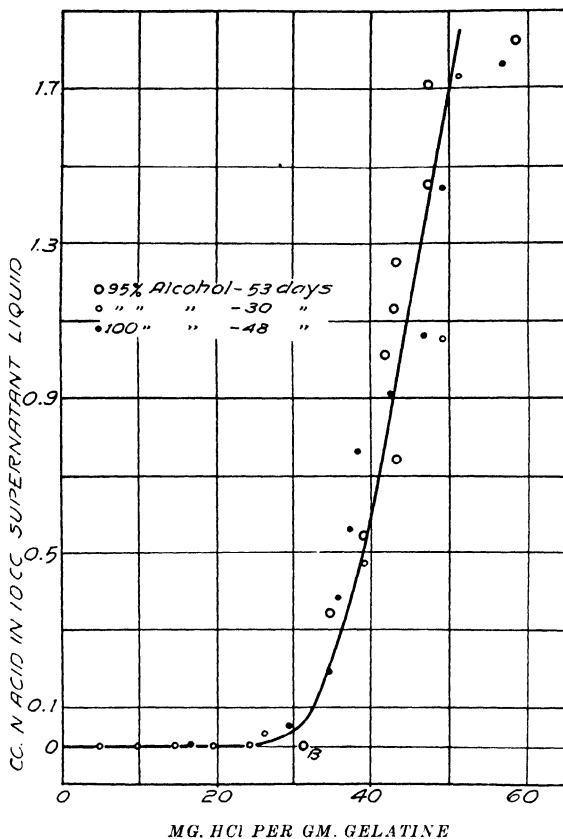
FIG. 9

Gelatine and HCl in 95% Ethyl Alcohol

2. *Gelatine*—The gelatine was from the Eastman Kodak Company, and was not further treated. It was from pig-skin, had a pH of 5.0, and was in the form of a powder.

Three runs with HCl were made. (See Tables XII-XIV and Fig. 9.) Both 95% and absolute ethyl alcohol were used. In the 95% alcohol, there

[1] J. Phys. Chem., **34**, 1071 (1930).

[2] Physiol. Rev., (2) **5**, 349 (1925).

[3] J. Gen. Physiol., **7**, 317 (1924-5).

[4] J. Gen. Physiol., **7**, 45 (1924-5).

[5] J. Phys. Chem., **14**, 528 (1910).

was considerable peptization in the higher numbers. In the absolute alcohol, there was practically none. Hydrolysis of the gelatine was less than 2.5% in each. The time of the runs was from a month to two months. The results of all of them fall very nicely on the same curve, showing that equilibrium is reached in the time allowed. A compound was formed and a little adsorption took place on it. It contained 25 mg. HCl per gm. of gelatine or 68×10^{-5} equivalents, and gelatine therefore has a combining weight of 1470 for strong acid. If point B on the curve is taken to represent the composition of the hydrochloride (and this does not seem unreasonable), 86×10^{-5} equivalents are bound. This value agrees better with those obtained by other workers. Some of these are:

TABLE XII

Gelatine and HCl in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc.   Length of run—53 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. gelatine equiv. × 10⁻³ (a − c)/.886	e mg. HCl per gm. gelatine d × 36.46
1.	0.76	0.00	0.00	0.86	31.3
2.	1.52	0.34	0.68	0.95	34.8
3.	2.03	0.54	1.08	1.07	39.0
4.	2.54	0.74	1.49	1.18	43.2
5.	3.04	1.01	2.03	1.15	41.8
6.	3.30	1.13	2.25	1.18	43.0
7.	3.55	1.25	2.50	1.18	43.2
8.	4.06	1.45	2.91	1.30	47.4
9.	4.56	1.71	3.41	1.30	47.4
10.	5.07	1.82	3.65	1.61	58.5

TABLE XIII

Gelatine and HCl in 95% Ethyl Alcohol

A continuation of Table XIII, except that the length of the run is 30 days

No.	a	b	c	d	e
1.	0.00	0.00	0.00	0.00	00.0
2.	0.12	0.00	0.00	0.13	04.9
3.	0.24	0.00	0.00	0.27	09.7
4.	0.35	0.00	0.00	0.40	14.6
5.	0.47	0.00	0.00	0.53	19.4
6.	0.59	0.00	0.00	0.66	24.2
7.	0.71	0.03	0.07	0.72	26.3
8.	1.88	0.47	0.93	1.08	39.1
9.	3.29	1.05	2.10	1.35	49.3
10.	4.71	1.73	3.46	1.41	51.3

TABLE XIV

Gelatine and HCl in Absolute Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc.   Length of run—48 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid $b \times 2$	d cc. N acid used per gm. gelatine equiv. $\times 10^{-3}$ $(a - c)/.886$	e mg. HCl per gm. gelatine $d \times 36.46$
1.	0.41	0.002	0.004	0.46	16.6
2.	0.81	0.05	0.10	0.81	29.5
3.	1.22	0.19	0.38	0.95	34.6
4.	1.63	0.38	0.76	0.98	35.8
5.	2.03	0.56	1.13	1.03	37.4
6.	2.44	0.76	1.51	1.05	38.2
7.	2.85	0.91	1.81	1.17	42.5
8.	3.25	1.06	2.12	1.28	46.8
9.	4.07	1.44	2.87	1.35	49.2
10.	4.88	1.76	3.52	1.53	55.9

80×10^{-5} equivalents by Bugarszky and Liebermann[1] as recalculated by Cohn[2]

85×10^{-5} equivalents by Atkin and Douglas[3]

89×10^{-5} equivalents by A. E. Stearn[4]

92×10^{-5} equivalents from viscosity measurements by Bacon[5]

94×10^{-5} equivalents as the best value of many determinations by Loeb and by Hitchcock[6]

104×10^{-5} equivalents (of acid dye) by Chapman, Greenberg, and Schmidt[7]

113×10^{-5} equivalents by Wintgen and his associates[8]

130×10^{-5} equivalents by Procter and Wilson[9]

150×10^{-5} equivalents by Manabe and Matula[10]

300×10^{-5} equivalents by Lloyd and Mayes[11]

300×10^{-5} equivalents by Belden[12] using solid protein and gaseous HCl.

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[1] Pflüger's Archiv, **72**, 51 (1898).

[2] Physiol. Rev., **5**, 349 (1925).

[3] J. Soc. Leather Trades' Chem., **8**, 359, 528 (1924).

[4] J. Gen. Physiol., **11**, 377 (1927-28).

[5] Ferguson and Bacon: J. Am. Chem. Soc., **49**, 1921, 1934 (1927); Bacon: J. Phys. Chem., **33**, 1843 (1929).

[6] J. Gen. Physiol., **4**, 733 (1921-22); **6**, 95, 201 (1923-24); **12**, 495 (1928-29).

[7] J. Biol. Chem., **72**, 707 (1927).

[8] Wintgen and Krüger: Kolloid-Z., **28**, 81 (1921); Wintgen and Vogel: **30**, 45 (1922).

[9] J. Chem. Soc., **109**, 307 (1916).

[10] Biochem. Z., **52**, 369 (1913).

[11] Proc. Roy. Soc., **93B**, 69 (1922).

[12] J. Phys. Chem., **35**, 2164 (1931).

In an attempt to duplicate the work of Belden who obtained a much higher value for the amount of acid bound by gelatine, the run in absolute alcohol was made. It was thought that perhaps the presence of water hindered the binding of the acid, but as previously noted, the result was the same as in 95% ethyl alcohol. In a further effort to duplicate Belden's results much stronger HCl (up to 4 N) in absolute alcohol was used. Even this relatively high concentration of HCl caused no more compound formation. There are some indications that alcohol is adsorbed by the protein, and for the present we must postulate this as the most likely explanation of the different results.
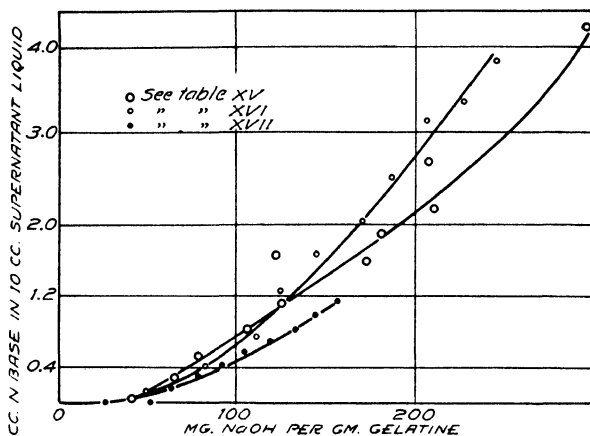
FIG. 10

Gelatine and NaOH in 95% Ethyl Alcohol

Three runs with NaOH in 95% ethyl alcohol were made. (See Tables XV-XVII and Fig. 10.) Peptization was considerable and became nearly complete in the more alkaline numbers. Two of the runs contained a large excess of alkali. Hydrolysis of the gelatine in the most alkaline numbers of these was about 40%, and was 17-18% in the most alkaline number of the third. The first two runs lasted two weeks and the other lasted nearly four. One of the first two was on a different sample of gelatine. The curves for all three coincide fairly well in the lower ranges, but the third soon shows the result of greater hydrolysis due to its longer standing. There is indication of the formation of a compound, but it is hard to judge accurately the amount of base bound in it due to the high hydrolysis. It contains about 30 mg. NaOH or 75×10^{-5} equivalents per gm. of gelatine, thus giving it a combining weight with strong alkalies of 1330. Another run with NaOH was made using about a 50% mixture of benzene and 95% ethyl alcohol as solvent. In all numbers of this run, all the NaOH was used up. This must be due to hydrolysis, which was very high—36%—even though the concentration of the alkali was no higher than usual, or we would be faced with the necessity of explaining a compound containing more than 530×10^{-5} equivalents of NaOH.

TABLE XV

Gelatine and NaOH in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc.   Length of run—14 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid $b \times 2$	d cc. N base used per gm. gelatine equiv. $\times 10^{-3}$ $(a - c)/.886$	e mg. NaOH per gm. gelatine $d \times 40.008$
1.	0.00	0.00	0.00	0.00	00.0
2.	1.00	0.04	0.09	1.03	41.2
3.	2.00	0.28	0.55	1.63	65.2
4.	3.00	0.52	1.03	2.22	89.0
5.	4.00	0.82	1.65	2.66	106.1
6.	5.00	1.11	2.22	3.14	125.4
7.	6.01	1.65	3.30	3.05	121.9
8.	7.01	1.59	3.17	4.32	172.9
9.	8.01	1.89	3.77	4.78	180.9
10.	9.01	2.17	4.34	5.26	210.5
11.	10.01	2.70	5.40	5.20	207.8
12.	15.01	4.21	8.43	7.43	296.8

TABLE XVI

Gelatine and NaOH in 95% Ethyl Alcohol

The same as Table XVI except on slightly different sample of gelatine

No.					
1.	1.31	0.12	0.24	1.23	49.1
2.	2.62	0.40	0.80	2.06	82.2
3.	3.93	0.74	1.47	2.77	110.9
4.	5.24	1.24	2.47	3.12	125.0
5.	6.55	1.67	3.34	3.62	144.8
6.	7.86	2.04	4.09	4.27	170.3
7.	9.17	2.52	5.04	4.66	186.5
8.	10.48	2.96	5.91	5.16	206.3
9.	11.79	3.37	6.75	5.69	227.6
10.	13.10	3.83	7.65	6.15	246.0

TABLE XVII

Gelatine and NaOH in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc.   Length of run—25 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. gelatine equiv. × 10^{-3} (a − c)/.886	e mg. NaOH per gm. gelatine d × 40.008
1.	0.58	0.00	0.00	0.65	26.0
2.	1.15	0.00	0.00	1.30	51.9
3.	1.73	0.16	0.32	1.58	63.3
4.	2.30	0.29	0.57	1.95	78.1
5.	2.88	0.42	0.84	2.30	91.8
6.	3.45	0.57	1.14	2.61	104.2
7.	4.03	0.69	1.39	3.00	119.1
8.	4.60	0.82	1.64	3.34	133.6
9.	5.18	0.99	1.98	3.60	144.1
10.	5.75	1.14	2.28	3.91	156.6

Some results recorded for gelatine and NaOH are:

56-7 × 10^{-5} equivalents by Loeb and by Hitchcock[1] as recalculated by Cohn[2]

60× 10^{-5} equivalents at a pH of 11 by Greenberg and Schmidt[3]

70-1 × 10^{-5} equivalents (of basic dye) by A. E. Stearn[4] and Rawlins and Schmidt[5]

74 × 10^{-5} equivalents by A. E. Stearn[6]

85 × 10^{-5} equivalents by Atkin and Douglas[7]

130 × 10^{-5} equivalents by Procter and Wilson[8]

2000 × 10^{-5} equivalents by Lloyd and Mayes[9]

3. *Zein*—The zein was very kindly sent to this department by Mr. H. B. Vickery of the Connecticut Agricultural Experiment Station.

With HCl in 95% ethyl alcohol, zein showed no compound formation, but considerable adsorption. (See Table XVIII and Fig. 11.) This result was also obtained by Bancroft and Barnett.[10] It is to be expected from the fact that zein is acidic, since it contains dicarboxylic amino acids and no free amino groups.   Hoffman and Gortner[11] who say that it combines with

[1] J. Gen. Physiol., **6**, 457 (1923-24).

[2] Physiol. Rev., **5**, 349 (1925).

[3] Proc. Soc. Exp. Biol. Med., **21**, 281 (1923-24).

[4] J. Biol. Chem., **91**, 325 (1931).

[5] J. Biol. Chem., **82**, 709 (1929).

[6] J. Gen. Physiol., **11**, 377 (1927-28).

[7] J. Soc. Leather Trades' Chem., **8**, 359, 528 (1924).

[8] J. Chem. Soc., **109**, 307 (1916).

[9] Proc. Roy. Soc., **93B**, 69 (1922).

[10] J. Phys. Chem., **34**, 449 (1930).

[11] Colloid Symp. Mon., **2**, 209 (1925).

20×10^{-5} equivalents of HCl at a pH of 2.5 and a maximum of 65×10^{-5} equivalents, are the only authors who have mentioned a compound with acid. There was very considerable solution of the zein. It is a prolamine which is soluble in solutions with a higher percentage of alcohol than most of them. The hydrolysis of the zein was about two percent.

With NaOH in 95% ethyl alcohol, there was complete solution or peptization and 25-30% hydrolysis of the zein. Although the upper part of the curve is undoubtedly displaced far to the right, the first few points where hydrolysis was very much less, show that a compound was formed. (See
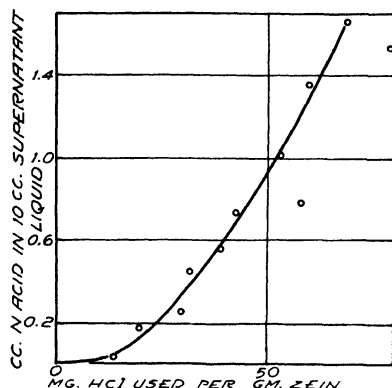
FIG. 11

Zein and HCl in 95% Ethyl Alcohol

TABLE XVIII

Zein and HCl in 95% Ethyl Alcohol

1 gm. zein, equivalent to .963 gm. dry zein, used in each number

Volume of each number—20 cc.   Length of run—21 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. zein equiv. × 10⁻³ (a − c)/.963	e mg. HCl per gm. zein d × 36.46
1.	0.43	0.03	0.07	0.37	13.6
2.	0.86	0.17	0.34	0.54	19.6
3.	1.28	0.25	0.51	0.81	29.3
4.	1.71	0.44	0.88	0.86	31.5
5.	2.14	0.56	1.12	1.06	38.7
6.	2.57	0.73	1.45	1.15	42.1
7.	3.08	0.78	1.55	1.58	57.7
8.	3.42	1.01	2.03	1.45	52.7
9.	4.28	1.35	2.70	1.63	59.5
10.	5.13	1.53	3.05	2.16	78.6
11.	5.13	1.66	3.33	1.87	68.3

The d column header note reads: equiv. × 10⁻³ i.e. $\text{equiv.} \times 10^{-3}$

Table XIX and Fig. 12.)   It contained approximately 28 mg. NaOH per gm. of zein, or 70 × 10^{-5} equivalents, and gives zein a combining weight with NaOH of 1430.   Cohn, Berggren, and Hendry[1] found less NaOH bound— 30 × 10^{-5} equivalents.   Hoffman and Gortner[2] report 20 × 10^{-5} equivalents bound at pH values of 10.2 and 10.5, and a maximum binding of 1400 × 10^{-5} equivalents.
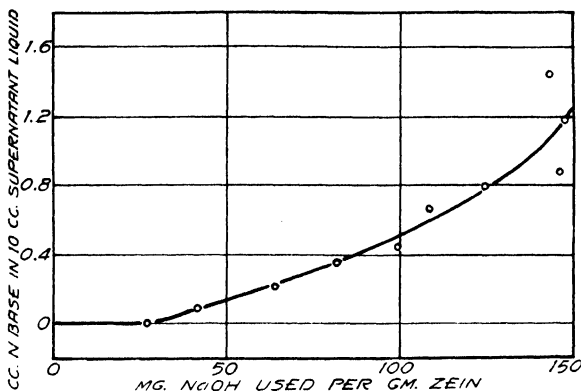
FIG. 12

Zein and NaOH in 95% Ethyl Alcohol

TABLE XIX

Zein and NaOH in 95% Ethyl Alcohol

1 gm. zein, equivalent to .963 gm. dry zein, used in each number
Volume of each number—20 cc.   Length of run—35 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. zein equiv. × 10^{-3} (a − c)/.963	e mg. NaOH per gm. zein d × 40.008
1.	0.66	0.00	0.00	0.68	27.2
2.	1.31	0.09	0.19	1.17	46.6
3.	1.97	0.21	0.42	1.60	64.0
4.	2.62	0.33	0.66	2.04	81.5
5.	3.28	0.44	0.88	2.49	99.5
6.	3.93	0.66	1.32	2.71	108.5
7.	4.59	0.79	1.59	3.11	124.5
8.	5.24	0.87	1.73	3.64	145.7
9.	5.90	1.18	2.35	3.67	147.1
10.	6.55	1.41	2.82	3.86	154.8
11.	6.33	1.44	2.88	3.58	143.0

[1] J. Gen. Physiol., 7, 81 (1924-5).
[2] Colloid Symp. Mon., 2, 209 (1925).

Because zein went into solution almost completely in the 95% ethyl alcohol, runs were tried in 85% acetone. This seemed to be an ideal solvent for Foreman[1] says that it may be substituted for 95% alcohol in titrating amino and carboxyl groyps, and Galeotti and Giampalmo[2] say that zein is insoluble in water-acetone mixtures. But there was still considerable peptization of the zein in the acid and alkaline acetone. The hydrolysis of the
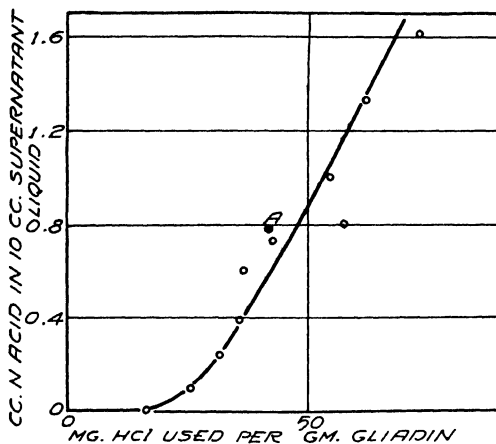
FIG. 13
Gliadin and HCl in 95% Ethyl Alcohol

zein was 15% in acid and 20% in alkali. The run with NaOH got very dark brown, so that the end-points were very poor; and the run with HCl had poor end-points, although the solutions were clear. With HCl the first part of the curve was the same as the one in 95% alcohol. Then the increased hydrolysis of the zein in acetone became apparent in a break in the curve which veered far to the right. With alkali, apparently much more was taken up in the form of a compound than in alcohol. We are inclined to doubt this. These runs in acetone were far from satisfactory.

4. *Gliadin*—The gliadin was a gift to this department from Professor R. A. Gortner of the University of Minnesota.

With HCl in 95% ethyl alcohol, gliadin did not peptize and hydrolyzed to the extent of about 1.4%. Contrary to expectations, it showed absolutely no indication of compound formation. (See Table XX and Fig. 13.) Bancroft and Barnett[3] obtained a curve with three flats and therefore showing three compounds, or at least three different pressures of HCl necessary for the formation of one or more compounds. In order to show whether our curve represented the true result under the conditions of our experiment, or whether it was lack of equilibrium, we made gliadin hydrochloride by the method of Bancoft and Barnett. This was put into 95% ethyl alcohol. It lost HCl until it reached a point (A-Fig. 13) on our curve, which must, therefore, be correct.

[1] Biochem. J., 14, 451 (1920).
[2] Kolloid-Z., 3, 118 (1908).
[3] J. Phys. Chem., 34, 449 (1930).

TABLE XX

Gliadin and HCl in 95% Ethyl Alcohol

1 gm. gliadin, equivalent to .946 gm. dry gliadin, used in each number
Volume in each number—20 cc.   Length of run—30 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid $b \times 2$	d cc. N acid used per gm. gliadin equiv. $\times 10^{-3}$ $(a - c)/.946$	e mg. HCl per gm. gliadin $d \times 36.46$
1.	0.43	0.003	0.007	0.44	16..2
2.	0.86	0.10	0.20	0.69	25.3
3.	1.28	0.24	0.48	0.86	31.4
4.	1.71	0.39	0.79	0.98	35.7
5.	2.14	0.60	1.20	0.99	36.3
6.	2.57	0.73	1.46	1.17	42.5
7.	3.08	0.80	1.60	1.57	57.2
8.	3.42	1.00	2.00	1.51	54.9
9.	4.28	1.33	2.66	1.71	62.2
10.	5.13	1.61	3.23	2.01	73.3

Compounds of gliadin with acid have been reported to contain:

28 $\times$ 10^{-5} equivalents by Bracewell[1]

34 $\times$ 10^{-5} equivalents by Cohn[2]

40 $\times$ 10^{-5} equivalents at pH 2.5 by Hoffman and Gortner[3] and to bind a maximum of 600 $\times$ 10^{-5} equivalents

184, 288, and 387 $\times$ 10^{-5} equivalents in three compounds by Bancroft and Barnett.[4]

With NaOH in 95% ethyl alcohol, there was some peptization and 14% hydrolysis of the gliadin. A compound (see Table XXI and Fig. 14) was formed which had 25 mg. or 62 $\times$ 10^{-5} equivalents of base per gm. gliadin. The combining weight with NaOH is then 1600. Some values given for the binding of alkali by gliadin are:

20 $\times$ 10^{-5} equivalents by Woodman[5]

30 $\times$ 10^{-5} equivalents by Greenberg and Schmidt[6] and Cohn[2]

20 $\times$ 10^{-5} equivalents at pH values of 10.2 and 10.5 and a maximum of 1300 $\times$ 10^{-5} equivalents by Hoffman and Gortner.[7]

[1] J. Am. Chem. Soc., 41, 1511 (1919).
[2] Physiol. Rev., 5, 349 (1925).
[3] Colloid Symp. Mon., 2, 209 (1925).
[4] J. Phys. Chem., 34, 449 (1930).
[5] J. Agri. Science, 12, 231 (1922).
[6] Proc. Soc. Expt. Biol. Med., 21, 281 (1924).
[7] Colloid Symp. Mon., 2, 209 (1925).
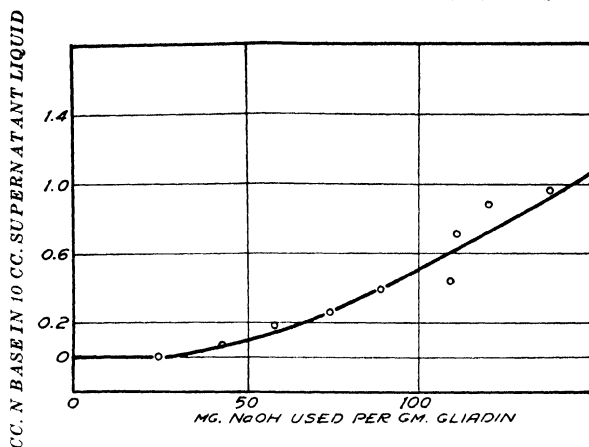
FIG. 14

Gliadin and NaOH in 95% Ethyl Alcohol

TABLE XXI

Gliadin and NaOH in 95% Ethyl Alcohol

1 gm. gliadin, equivalent to .946 gm. dry gliadin, used in each number

Volume in each number—20 cc. Length of run—30 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. gliadin equiv. × 10^{-3} (a − c)/.946	e mg. NaOH per gm. gliadin d × 40.008
1.	0.58	0.00	0.00	0.61	24.3
2.	1.15	0.07	0.15	1.06	42.5
3.	1.73	0.18	0.37	1.44	57.5
4.	2.30	0.28	0.55	1.85	74.0
5.	2.88	0.39	0.78	2.22	88.8
6.	3.45	0.44	0.88	2.72	108.7
7.	4.03	0.71	1.41	2.76	110.6
8.	4.60	0.88	1.77	3.00	119.9
9.	5.18	0.96	1.92	3.44	137.7
10.	5.75	0.97	1.93	4.04	161.7

5. *Edestin*—Edestin was purchased from Eimer and Amend and used as it was bought.

With HCl in 95% ethyl alcohol, there was no peptization and about 1.4% hydrolysis of the edestin. A compound (see Table XXII and Fig. 15) was formed with 45 mg. or 124 × 10^{-5} equivalents of HCl per gm. of edestin; or edestin has a combining weight of 810. Other values for the binding of acid by edestin are:

18×10^{-5} equivalents as the amount of strong monobasic acid required to dissolve 1 gm. edestin by Hardy[1]

14×10^{-5} equivalents necessary to "saturate" acid with edestin by Osborne[2b]

115×10^{-5} equivalents at pH 2.5 by Sandstrom[3]

127×10^{-5} equivalents by Cohn[4] as the best value recalculated from Hitchcock,[5a, b] Kodama,[6] and Osborne.[2a]

130×10^{-5} equivalents using tropaeolin as indicator by Osborne.[2a]

134×10^{-5} equivalents as his best value by Hitchcock.[5a, b, c]

250×10^{-5} equivalents by Bancroft and Barnett.[7]

TABLE XXII

Edestin and HCl in 95% Ethyl Alcohol

1 gm. edestin, equivalent to .928 gm. dry edestin, used in each number

Volume in each number—20 cc.   Length of run—31 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. edestin equiv. × 10^{-3} (a − c)/.928	e mg. HCl per gm. edestin d × 36.46
1.	0.43	0.00	0.00	0.46	16.8
2.	0.86	0.00	0.00	0.92	33.6
3.	1.28	0.04	0.08	1.27	46.2
4.	1.71	0.23	0.46	1.35	49.1
5.	2.14	0.39	0.79	1.46	53.1
6.	2.57	0.55	1.10	1.58	57.6
7.	3.08	0.80	1.60	1.60	58.2
8.	3.42	1.00	2.00	1.53	55.9
9.	4.28	1.36	2.73	1.67	60.8
10.	5.13	1.76	3.53	1.73	63.0

[1] J. Physiol., **33**, 251 (1905).

[2] (a) J. Am. Chem. Soc., **21**, 486 (1899); (b) **24**, 39 (1902).

[3] J. Phys. Chem., **34**, 1071 (1930).

[4] Physiol. Rev., **5**, 349 (1925).

[5] (a) J. Gen. Physiol., **4**, 597 (1921-22); (b) **5**, 383 (1922-3); (c) **14**, 99 (1930-31).

[6] J. Biochem. (Japan), **1**, 419 (1922).

[7] J. Phys. Chem., **34**, 449 (1930).
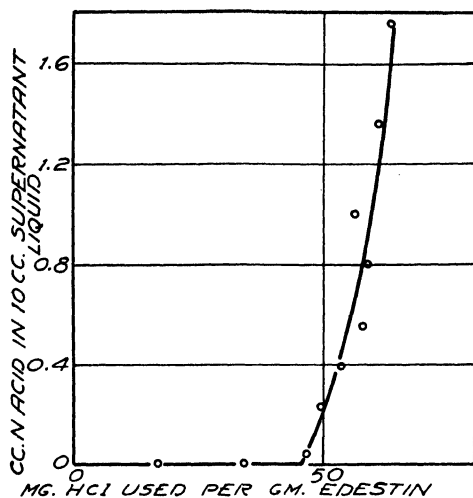
FIG. 15

Edestin and HCl in 95% Ethyl Alcohol

TABLE XXIII

Edestin and NaOH in 95% Ethyl Alcohol

1 gm. edestin, equivalent to .928 gm. dry edestin, used in each number

Volume in each number—20 cc.   Length of run—31 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. edestin equiv. × 10^{-3} (a − c)/.928	e mg. NaOH per gm. edestin d × 40.008
1.	0.58	0.00	0.00	0.62	24.8
2.	1.15	0.02	0.04	1.19	47.7
3.	1.73	0.12	0.24	1.60	64.0
4.	2.30	0.23	0.45	1.99	79.7
5.	2.88	0.34	0.68	2.37	94.6
6.	3.45	0.31	0.63	3.04	121.7
7.	4.03	0.63	1.25	2.99	119.6
8.	4.60	0.74	1.48	3.36	134.6
9.	5.18	0.93	1.87	3.56	142.5
10.	5.75	1.11	2.22	3.80	152.0

With NaOH in 95% ethyl alcohol, there was no peptization. There was 11% hydrolysis of the edestin. A compound was formed (see Table XXIII and Fig. 16) on which the hydrolysis made the curve appear to represent a large amount of adsorption. The compound had 43 mg. or 108 × 10^{-5}
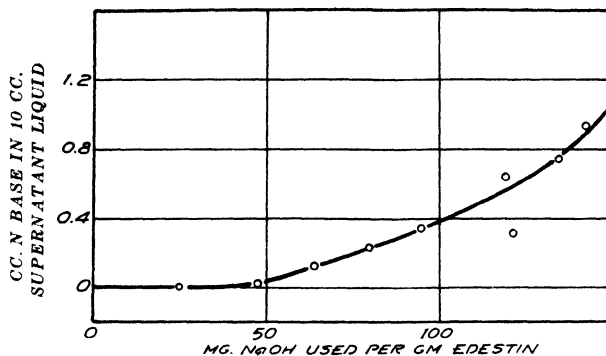
Fig. 16

Edestin and NaOH in 95% Ethyl Alcohol

equivalents of NaOH per gm. edestin, and therefore gives the protein a combining weight of 925. Other values for edestin and alkali are:

10 $\times$ 10^{-5} equivalents as necessary to dissolve edestin by Hardy[1]

7 $\times$ 10^{-5} equivalents to "saturate" alkali with edestin by Osborne[2]

36 $\times$ 10^{-6} equivalents at pH 10.5 by Sandstrom[3]

75 $\times$ 10^{-5} equivalents by Kodama[4] as recalculated by Cohn[5]

90 $\times$ 10^{-5} equivalents by Hitchcock[6] as recalculated by Cohn[5]

Summary

1. The phase rule method of studying proteins, developed by Bancroft and Barnett, has been extended to apply to acids and bases dissolved in a solvent, chemically inert to the system, which does not dissolve the protein or its product with acid or base.

2. The method of titrating excess strong acid or base in alcoholic solution in the presence of weak acids or bases, using thymolphthalein and thymol blue, has been applied to peptized proteins and their hydrolysis products.

3. Succinic acid, used as a test of the method, was found to form a mono- and a di-sodium salt.

4. Uric acid formed a mono- and a di-sodium salt; and in the presence of excess alkali, formed a tri- and a tetra-sodium salt. These formed much more readily in 95% isobutyl than in 95% ethyl alcohol. The presence of a small percent of water in the alcohol hastened the formation of the compounds but was not necessary to it.

[1] J. Physiol., **33**, 251 (1905).

[2] J. Am. Chem. Soc., **24**, 39 (1902).

[3] J. Phys. Chem., **34**, 1071 (1930).

[4] J. Biochem. (Japan), **1**, 419 (1922).

[5] Physiol. Rev., **5**, 349 (1925).

[6] J. Gen. Physiol., **4**, 597 (1921-22).

5. Uracil formed a compound with one equivalent of NaOH in 95% ethyl alcohol. With HCl, no compound formed, and there was very little adsorption.

6. Alanine formed a compound with one equivalent of NaOH and another with one equivalent of HCl.

7. Casein, gelatine, and edestin showed compound formation with HCl in ethyl alcohol. Zein and gliadin showed only adsorption with HCl.

8. Casein, gelatine, zein, gliadin, and edestin showed possible compound formation with NaOH in ethyl alcohol plus marked adsorption, or adsorption alone with the adsorption practically complete at the lower concentrations.

9. In general, less HCl was taken up from contact with an alcoholic solution than from contact with gaseous HCl.

Cornell University.

EXTINCTION COEFFICIENTS OF THE SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

Lord Rayleigh has derived mathematically an expression according to which I, the intensity of light scattered by a colloidal solution at right angles to the incident beam is proportional to n, the number of particles per unit volume and to the square of v, the volume of the particle i.e.

$$I = \frac{Knv^2}{\lambda}$$

where K is a constant and λ will be constant if the same source of light is used.

Since c, the concentration of the colloid is given by $nv\rho$, where ρ is the density of the colloidal matter,

$$I = \frac{kcv}{\rho}$$

That is, at constant concentration the intensity of the scattered light is proportional to the volume of the particles. This expression does not apply to concentrated sols and to the sols in which the particles are not optically isotropic.

Mie[1] has studied the absorption and scattering of light by colloidal solutions containing particles of various dimensions and has concluded that at constant concentration the intensity of the diffused light increases with the size of the particles and is proportional to their volume.

Krishnamurti[2] has emphasized the importance of the study of the optical properties of colloidal solutions as they reveal their structure without disturbing their internal equilibrium. He has studied the scattering of light by agar sols and gels and has found that the micelles in the gels are much bigger than those in the sols.

In the present investigation the scattering of light from the silicic acid gel-forming mixtures has been studied during the process of gel-formation. The intensity of scattered light has been determined from the measurements of the extinction coefficients of these mixtures and the results obtained have been utilised in elucidating the changes in size and number of the colloidal particles which take place in these mixtures during the gel-formation.

Experimental

The extinction coefficients were measured by means of Nutting's photometer used in conjunction with the Hilger wave-length spectrometer.

[1] Ann. Physik, 25, 377 (1908).
[2] Proc. Roy. Soc., 122 A, 76 (1929).

Light from a 50 c.p. point-o-lite lamp was divided into two beams by a pair of prisms placed at a distance of 19 cms from the lamp. The two beams of light were incident on the two apertures of the Nutting's photometer after emerging from which they fell on the slit of the spectrometer and were re-franged into three consecutive spectral bands of light. The different parts of the apparatus were accurately aligned with each other to avoid diffraction bands from obliterating the field of vision.

The nicol of the photometer was then adjusted so that the logarithmic scale on the disc of the photometer read zero when an empty rectangular glass cell, used to hold the gel-forming mixture, was interposed in the path of one of the beams. This was done with a view to eliminate any initial absorption due to the glass cell.

The gel-forming mixture was placed in the cell and the equality of the intensity of the three spectra in the green region ($\lambda = 5430 \ \mu\mu$) was restored by turning the disc of the photometer. The rotation read on the logarithmic scale, is equal to log I_o/I where I_o is the original intensity of the beam and I that of the beam transmitted through the mixture. Values of the extinction coefficient were obtained by dividing log I_o/I by t, the thickness of the gel-forming mixture.

Solution of sodium silicate was prepared by keeping a large quantity of Merck's extra pure dry sodium silicate ($Na_2O.2.5SiO_2$) in contact with redistilled water for three days. It was then twice filtered and kept in a well stoppered Jena glass flask. It was found that this solution underwent no change in concentration for about six months. The strength of the solution was determined by analysis and has been expressed in grams of silica per 100 c.c. of the solution.

Solution of acidic ammonium acetate which was first used for the preparation of gels[11] was prepared by dissolving a large quantity of Kahlbaum's extra pure ammonium acetate in redistilled water with the addition of a little acid to it. On analysis this solution was found to contain 39.99% free acetic acid. Solutions of acetic acid used later were prepared from Merck's extra pure product.

Equal volumes of solutions of sodium silicate and of acidic ammonium acetate or of acetic acid were thoroughly mixed in a test tube and transferred to the cell, which was thoroughly cleaned and dried beforehand. The stop-watch was started simultaneously with the mixing of the solutions and readings on the logarithmic scale of the photometer were taken at definite intervals after mixing.

The results obtained are given in the following tables and one set of the curves between the extinction coefficient and time is shown in Fig. 1. The reaction of these mixtures towards litmus has been tested and the pH values of some of them have also been measured by the colorimetric method.

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[11] Cf. Prasad and Hattiangadi: J. Indian Chem. Soc., **6**, 653 (1929).

TABLE I

Silica Content 3%

Time	Concentration of ammonium acetate			
	3%	4% Alkaline	5%	6% Acidic
1′ 0″	0.009993	0.1089	0.1579	0.03996
1′30″	0.04396	0.1659	0.1859	0.08794
3′ 0″	0.1140	0.1899	0.1859	0.1599
6′ 0″	0.1599	0.1899		0.1698
10′ 0″	0.1739			0.1819
15′ 0″	0.1819			0.1819
20′ 0″	0.1819			

	7%	8% Acidic	10%
1′ 0″	0	0.003996	0
3′ 0″	0.003996	0.007995	0
9′ 0″	0.04396	0.009995	0.001998
13′ 0″	0.084	0.01399	0.005995
23′ 0″	0.1379	0.01998	0.007995
38′ 0″	0.1539	0.05597	0.01199
56′ 0″	0.1539	0.09792	0.01799
70′ 0″		0.1219	0.03396
90′ 0″		0.1359	0.06195
104′ 0″		0.1419	0.07995
120′ 0″		0.1419	0.092

TABLE II

Silica Content 4%

Time	Concentration of ammonium acetate				Time	Concentration of ammonium acetate	
	3%	4% Alkaline	9%	10% Acidic		15%	20% Acidic
1′ 0″	0.01998	0.1739	0.01199	0.01199	1′ 0″	0	0
2′ 0″	0.07394	0.1819	0.03396	0.03396	2′ 0″	0.01199	0
2′45″	0.1279	0.1958	0.07995	0.05995	8′ 0″	0.01399	0.001998
7′ 0″	0.1759	0.1958	0.1579	0.1079	25′ 0″	0.01998	0.005995
8′ 0″	0.1819		0.1599	0.1199	45′ 0″	0.02798	0.009993
13′ 0″	0.1819		0.1719	0.1479	60′ 0″	0.05795	0.01799
14′ 0″			0.1739	0.1539	72′ 0″	0.06995	0.02202
21′ 0″			0.1739	0.1819	96′ 0″	0.09994	0.04796
22′ 0″				0.1859	114′ 0″	0.1159	0.07396
26′ 0″				0.1859	120′ 0″	0.1219	0.07794

TABLE III

Silica Content 3%

Time	Concentration of acetic acid			
	0.331 N	0.34 N	0.36 N	0.397 N
	Alkaline		Acidic	
1' 0"	0	0.01998	0	0
4' 0"	0.007995	0.02598	0.03198	0.001998
14' 0"	0.04197	0.06395	0.08392	0.007995
24' 0"	0.07396	0.09393	0.1339	0.01079
35' 0"	0.1020	0.1159	0.1419	0.02598
41' 0"	0.1059	0.1239	0.1419	0.03198
54' 0"	0.1239	0.1319		0.04796
73' 0"	0.1299	0.1319		0.07595
79' 0"	0.1319			0.08596
99' 0"	0.1319			0.1099
109' 0"				0.1140
115' 0"				0.1140

TABLE IV

Silica Content 4%

Time	Concentration of acetic acid			
	0.373 N pH (9)	0.397 N (8.1)	0.55 N (5−3)	0.60 N (5.2)
1' 0"	0.009993	0.04796	0.01399	0.01399
11' 0"	0.02798	0.09993	0.01399	0.01599
28' 0"	0.05196	0.1559	0.02598	0.01998
42' 0"	0.06998	0.1719	0.04596	0.02598
48' 0"	0.07596	0.1739	0.05597	0.03198
62' 0"	0.09194	0.1739	0.07995	0.04197
85' 0"	0.1119		0.1159	0.06395
98' 0"	0.1219		0.1298	0.07595
106' 0"	0.1239		0.1359	0.08392
118' 0"	0.1239		0.1399	0.09194
120' 0"			0.1399	0.09592

TABLE V

Silica Content 5%

Time	Concentration of acetic acid			
	0.45 N pH (9.15)	0.50 N (7.5)	0.67 N (5.3)	8.70 N (5.2)
1′ 0″	0.03198	0.1119	0.01399	0.01399
4′ 0″	0.03597	0.1819	0.02997	0.01799
6′ 0″	0.03597	0.1998	0.03797	0.02198
16′ 0″	0.04098	0.1998	0.08794	0.03597
29′ 0″	0.05196		0.1459	0.07794
43′ 0″	0.06395		0.1639	0.1199
48′ 0″	0.07194		0.1679	0.1299
68′ 0″	0.09194		0.1679	0.1539
92′ 0″	0.1099			0.1659
103′ 0″	0.1159			0.1679
110′ 0″	0.1219			0.1679
115′ 0″	0.1239			0.1679
120′ 0″	0.1259			

Discussion of Results

It will be seen from the curves (Fig. 1) that in each case the extinction coefficient of the gel-forming mixture increases with time at first slowly, then rather rapidly and finally more slowly until it reaches an almost constant value, when the curves run parallel to the time-axis. This indicates that the value of log. I or I continuously decreases, that is, the intensity of the scattered light increases with time. These curves, therefore, represent the manner in which the size of the particles of the gel increases during the process of gel formation.

The extinction coefficients of the various gel-forming mixtures have been measured from the time of mixing the gel forming constituents until the mixtures set to a gel. Prasad and Hattiangadi[1] have shown that when the gel forming constituents are mixed, a sol of silicic acid is first formed and the gel is formed from the coagulation of the sol. These observations, therefore, include those of the sols in the beginning and of the gels in the end. The higher values of the extinction coefficient in gels than in the corresponding sols definitely show that the particles in the gel are bigger in size than in the sol. Also the continuous nature of the curves indicates that in the gel forming mixtures the formation of the colloidal particles, their growth in size and increase in hydration and the final coalescence of these hydrated particles, resulting in the formation of definite structures, are continuous processes.

From study of different properties of soap sols and gels McBain[2] concludes that the colloidal particles in the sol and the gel state are identical in

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[1] J. Indian Chem. Soc., 6, 893 (1929).
[2] J. Chem. Soc., 117, 1506 (1920).

nature and amount: gels differ from sols only in possessing elastic properties. This view is, however, not supported by the conclusions mentioned above, according to which the formation of the bigger particles by the union of the smaller ones appears to be a necessary factor in the sol gel transformation.

FIG. I
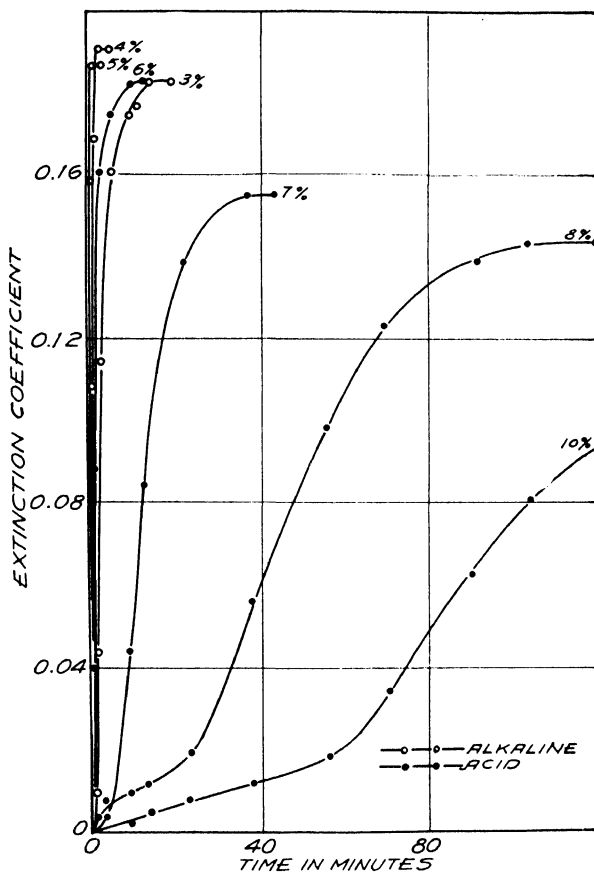
Silica Content: 3% (with ammonium acetate)

Krishnamurti[1] has also come to the same conclusion from the study of the agar sols and gels.

Further it will be seen from Tables VI and VII that at the time of setting the extinction coefficients of alkaline gels are higher than those of the acidic ones, that is, the light scattered by the former gels is greater than that by the latter. Considering the gels containing the same concentration of silica it appears that the particles formed in the alkaline gels are bigger in size than those formed in the acidic ones and hence the alkaline gels appear more opalescent than the acidic ones.[2]

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[1] Loc cit.

[2] Cf. Prasad and Hattiangadi: loc. cit. p. 653.

TABLE VI

Extinction coefficient at the time of setting

Concentration of ammonium acetate	Silica content	
	3%	4%
4%	0.1899 (alk)	0.1958 (alk)
5%	0.1859 "	—
6%	0.1819 "	—
7%	0.1539 (acidic)	—
8%	0.1419 "	—
9%	—	0.1739 (acidic)
10%	—	0.1859 "

TABLE VII

Extinction coefficient at the time of setting

Concentration of acetic acid	Silica content		
	3%	4%	5%
0.331 N	0.1319 (alk)	—	—
0.34 N	0.1319 "	—	—
0.36 N	0.1419 "	—	—
0.373 N	—	—	—
0.397 N	0.1140 (acidic)	0.1739 (alk)	—
0.50 N	—	—	0.1998 (alk)
0.55 N	—	0.1399 (acidic)	—
0.67 N	—	—	0.1679 (acidic)
0.70 N	—	—	0.1679 "

The conclusion regarding the size of the particles in alkaline and acidic gels is supported by the observation of Linder and Picton[1] who found no Tyndall cone in the dialysed sol of silicic acid in the presence of large concentration of hydrochloric acid.

It is also known that when hydrochloric acid is added to isoelectric gelatin, it gets positively charged and has a greater tendency to disintegrate than the iso-electric gelatin. Prasad and Hattiangadi[2] have shown that the silicic acid particles in the acidic mixtures are positively charged. Lösenbeck[3] has shown that the density of the positive charge in the silicic acid is much greater than the negative charge. The fineness of the particles in the acid mixture may, therefore, be due to the greater disintegration of the positively charged silicic acid in these mixtures.

It will be seen from the curves shown in Fig. 1 that they ultimately run parallel to the time-axis. This indicates that the changes involved in the

[1] J. Chem. Soc., 61, 154 (1892).

[2] Loc. cit. p. 893.

[3] Kolloidchem. Beihefte, 16, 27 (1922).

setting of the gel have reached a final stage. These measurements can, therefore, be used to determine the time of setting of gels.

The time of setting of silicic acid gels has been measured by Fleming[1] by the criterion that the set gel does not flow out of the container. Fells and Firth[2] have used the criterion of the pressure required to blow a bubble through the gel forming mixture. Prasad and Hattiangadi[3] have calculated the time of setting from the intensity of light transmitted by the gel forming mixture at different intervals during gel formation. The times of setting from the present investigation are given below.

<div align="center">

TABLE VIII

(A) Silica Content 3%
</div>

Concentration of ammonium acetate	Alkaline			Acidic			
	3%	4%	5%	6%	7%	8%	10%
Time of setting	15′ 0″	3′ 0″	1′ 30″	10′ 0″	38′ 0″	116′ 0″	More than two hours

Concentration of acetic acid	0.33N		0.34N	0.36N		0.39N	
Time of setting	79′ 0″		55′ 0″	33′ 0″		109′ 0″	

<div align="center">

(B) Silica Content 4%
</div>

Concentration of ammonium acetate	Alkaline		Acidic		
	3%	4%	9%	10%	15%
Time of setting	8′ 0″	2′ 45″	14′ 0″	22′ 0″	More than two hours
Concentration of acetic acid	0.37 N	0.40 N	0.55 N		0.60 N

pH value	9	8.1	5.3	5.2
Time of setting	106′ 0″	48′ 0″	118′ 0″	More than two hours

<div align="center">

(C) Silica Content 5%
</div>

Concentration of acetic acid	0.45 N	0.50 N	0.67 N	0.70 N
pH value	9.15	7.5	5.3	5.2
Time of setting	More than two hours	6′ 0″	48′ 0″	110′ 0″

[1] Z. Physik, **41**, 427 (1902).
[2] Trans. Faraday Soc., **23**, 625 (1927).
[3] Loc. cit. p. 653.

The relative effect of the silica content, on the time of setting, is shown in the following table:

TABLE IX

(1) Concentration of ammonium acetate	3%		4%	
Silica content	3%	4%	3%	4%
Reaction	Alkaline		Alkaline	
Time of setting	15' 0"	8' 0"	3' 0"	3' 45"
(2) pH value	5.3		5.2	
Silica content	4%	5%	4%	5%
Time of setting	118' 0"	48' 0"	More than two hours	110' 0"

The time of setting of the gel, therefore, depends upon (i) the concentration of silica and (ii) the H ion concentration of the mixture: it decreases as the concentration of silica is increased, while, with an increase in the H ion concentration the time of setting at first decreases and then begins to increase.[1]

The mixtures having pH 6-8 set in minimum time. No extinction coefficient readings could be taken with mixtures within this range as they set in a very short time but the determination of the time of setting by Fleming's method confirmed the results of previous workers, that the mixtures setting in minimum time are either slightly alkaline or neutral.

Considering that the process of gel formation is one of coagulation of the sol[2] it would be interesting to examine the applicability of Smoluchowski's theory of kinetics of coagulation[3] to the case of silicic acid gel formation. The conditions of the theory require that the coagulation curves must be similar in shape and related to one another. This is indicated by the similarity of the curves shown in Fig. 1. If then a particular value of the extinction coefficient is shown by various mixtures at times t, t_2, t_3, $\Sigma\eta$ which represents the same stage of coalescence, has a fixed value and

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} = \frac{t_3}{T_3}$$

or $t_1 : t_2 : t_3 \dots \dots t_n = T_1 : T_2 : T_3 \dots \dots T_n$

where T_1, T_2, $T_3 \dots \dots T_n$ are constants. The ratio of T_1, T_2, T_3 must, therefore, be a fixed ratio independent of the absolute values of the extinction coefficients. These values are taken from the curves drawn for Tables I to V and are given in the following tables.

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[1] Cf. Prasad and Hattiangadi: loc. cit.

[2] Cf. Arisz: Kolloidchem. Beihefte, 7, 18 (1915); Prasad and Hattiangadi: loc. cit., p. 893; Dhar and Prakash: J. Indian Chem. Soc., 6, 391 (1929).

[3] Physik. Z., 17, 557 (1916); Z. physik. Chem., 92, 129 (1917).

TABLE X

Silica Content 3%

Ext. coeff.	Time in minutes with following concentrations of ammonium acetate							Ratios						
	3% t_1	4% t_2	5% t_3	6% t_4	7% t_5	8% t_6	10% t_7	$\frac{T_1}{T_3}$	$\frac{T_2}{T_3}$	T_3	$\frac{T_4}{T_3}$	$\frac{T_5}{T_3}$	$\frac{T_6}{T_3}$	$\frac{T_7}{T_3}$
0.04	1.45	0.5	0.45	1.0	8.5	32.5	74	3.22	1.1	1	2.22	18.88	72.2	164.4
0.06	1.8	0.6	0.55	1.25	10.6	40.0	88	3.27	1.09	1	2.24	19.27	72.22	160.0
0.07	2.0	0.7	0.6	1.35	11.5	44.0	96	3.3	1.17	1	2.25	19.7	73.34	160.0
0.09	2.45	0.8	0.75	1.5	13.6	53.0	116	3.26	1.07	1	2.0	18.14	70.66	154.67
0.10	2.63	0.9	0.8	1.6	14.75	57.0	—	3.29	1.13	1	2.0	18.44	71.25	—
0.11	2.9	1.0	0.85	1.7	16.0	62.0	—	3.41	1.18	1	2.0	18.82	72.94	—
0.12	3.2	1.05	0.90	1.75	17.75	68.0	—	3.55	1.17	1	1.94	19.7	75.56	—

TABLE XI

Silica Content 4%

Ext. coeff.	Time in minutes with the following concentrations of ammonium acetate						Ratios					
	3% t_1	4% t_2	9% t_3	10% t_4	15% t_5	20% t_6	$\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$	$\frac{T_5}{T_2}$	$\frac{T_6}{T_2}$
0.03	1.25	0.25	1.8	1.8	48	80	5.0	1	7.2	7.2	192	320
0.04	1.5	0.3	2.2	2.25	57	90	5.0	1	7.34	7.5	190	300
0.05	1.75	0.35	2.25	2.5	63	97	5.0	1	6.43	7.14	180	277.14
0.06	1.9	0.4	2.5	2.75	67	104	4.75	1	6.25	6.88	167.5	260
0.07	2.0	0.45	2.6	3.0	72	111	4.45	1	5.78	6.67	160	246.67
0.08	2.1	0.5	2.75	3.5	78	—	4.2	1	5.5	7.0	156	—
0.09	2.2	0.5	2.9	4.25	85	—	4.4	1	5.8	8.5	170	—

TABLE XII

Silica Content 3%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid				Ratios			
	0.33 N t_1	0.34 N t_2	0.36 N t_3	0.397 N t_4	$\dfrac{T_1}{T_3}$	$\dfrac{T_2}{T_3}$	T_3	$\dfrac{T_4}{T_3}$
0.04	12.5	9.0	0.8	47.5	1.56	1.13	1	5.94
0.05	15.5	11.0	9.5	55.5	1.63	1.16	1	5.84
0.06	19.0	13.0	10.5	62.5	1.81	1.24	1	5.95
0.07	22.5	15.5	12.0	69.5	1.88	1.29	1	5.79
0.08	26.0	18.5	13.0	75.5	2.0	1.42	1	5.81
0.09	31.0	22.0	14.0	81.5	2.21	1.57	1	5.82
0.10	36.0	26.0	16.5	88.0	2.12	1.58	1	5.34

TABLE XIII

Silica Content 4%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid				Ratios			
	0.373 N t_1	0.397 N t_2	0.55 N t_3	0.60 N t_4	$\dfrac{T_1}{T_2}$	T_2	$\dfrac{T_3}{T_2}$	$\dfrac{T_4}{T_2}$
0.06	34	6	50	81	5.67	1	8.34	13.5
0.07	42	7	56	91	6.0	1	8.0	13.0
0.08	51	8	61.5	101	6.38	1	7.69	12.63
0.09	61	9	67	113	6.78	1	7.45	12.56
0.10	71	11	74	—	6.45	1	6.73	—
0.11	81	12.5	80	—	6.48	1	6.4	—
0.12	95	15	87	—	6.34	1	5.8	—

TABLE XIV

Silica Content 5%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid			
	0.45 N t_1	0.50 N t_2	0.67 N t_3	0.70 N t_4
0.05	29.0	0.20	9.5	20.0
0.06	40.0	0.25	12.0	24.0
0.07	48.0	0.30	13.0	27.0
0.08	56.0	0.40	15.0	29.5
0.09	66.0	0.55	16.0	32.0

Ratios			
$\dfrac{T_1}{T_2}$	T_2	$\dfrac{T_3}{T_2}$	$\dfrac{T_4}{T_2}$
145	1	47.5	100
160	1	48.0	96
160	1	43.34	90
140	1	37.5	73.75
120	1	29.09	58.18

It will be seen from these tables that in most of the cases the range of variation in the values of T is small. This shows that the ratios of the values of T are almost independent of the time or the stage of gelation. It appears that within a certain range of extinction coefficients shown in the tables the gelation of silicic acid approximates to the case of an ideal coagulation assumed by Smoluchowski. It should however be noted that for very low or very high values of extinction coefficients the variations in the ratios are too great to be negligible.

Prasad and Hattiangadi[1] have pointed out that the colloidal particles of silicic acid are first formed after the gel-forming constituents are mixed. Krishnamurti[2] has followed the changes in the intensity of the Tyndall light with time during the hydrolysis of methyl silicate and has found that the primary particles first formed, grow into bigger aggregates. The continuity of the time-extinction coefficient curves, however, indicates that the formation of colloidal particles and their coagulation are taking place simultaneously. But it is reasonable to assume that in the beginning the rate of formation of the colloidal particles will be much greater than their coagulation. The discrepancy in the preliminary stage thus appears to be due to the simultaneous formation of colloidal particles.

In the later stage of gel-formation the discrepancy may be due to the high degree of hydration of the particles on account of which their collisions may not be perfectly inelastic and the assumptions of Smoluchowski's theory are not satisfied.

[1] Loc. cit. p. 893.
[2] Nature, 124, 690-691 (1929).

Summary

(1) The extinction coefficients of various mixtures forming gels of silicic acid have been measured by means of Hilger Nutting's spectro-photometer. It has been shown that at constant concentration the micelles in gels are bigger than those in sols. Also, at constant concentration the micelles in alkaline gels are bigger than in the acidic ones.

(2) The time of setting of the gels has been calculated from the curves in which extinction coefficients are plotted against time.

(3) Application of Smoluchowski's theory of kinetics of coagulation of a colloidal solution by electrolytes has been extended to the case of gelation.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

NEW BOOKS

Colloid Chemistry Theoretical and Applied. *Edited by Jerome Alexander. Vol. III. 23 × 17 cm; pp. 655. New York: Chemical Catalog Company, 1931. Price: $10.50.* In the preface the author says: "There is a wealth of wisdom in 'cooking recipes,' despite the fact that this term is sometimes used as an acme of scientific scorn. Time out of mind cooks have beaten the whites of eggs separately from the yolks, and secured light cake by carefully folding in the beaten leavening froth of the whites into the batter containing the yolks. The modern physical chemist finds that the lipoid or fatty matter in the yolks makes the foam bubbles of the beaten whole egg so unstable that if you beat up the whole egg 'your cake is all dough.' Furthermore, the use of oils or fats as 'foam killers' has long been 'rule-of-thumb' practice in many industries, and has also been frequently made use of by sea-captains. In fact, 'to throw oil on the troubled waters' has become proverbial.

"The upshot of these remarks is that scientists must consider the existence of a long-standing practice as presumptive evidence that there is *something* valuable in or about it and that exploration in that neighborhood, with impartial separation of gangue, should yield some nuggets of truth. Geologists frequently learn a great deal about the strata of certain regions by a careful examination of mineral grains in ant hills," p. 3.

"As to the arrangement of papers in Vols. III and IV, which conclude the series, the first group consists of subjects of interest to many industries, and comprises eleven papers on *general principles* and six papers dealing with *mechanical* or more specialized matters. The large second group (twenty-five papers) may, for want of a better name, be termed *telluric*; for it deals with matters which are of the earth, earthy, beginning with geology and mineralogy, and running to metals, petroleum, asphalt and agriculture," p. 5.

The papers and authors are: Cohesion and Adhesion by J. W. McBain and Jerome Alexander; Some Practical Results of X-ray Researches on Colloids by G. L. Clark; Wetting of Solids by F. E. Bartell; Spontaneous Dispersion of Small Liquid Particles by N. Rashevsky; The Influence of Elasticity and Permeability on the Swelling of Two-Phase Systems by Karl von Terzaghi; On the Rubber-like and Liquid-Crystalline States of Matter, in Connection with the Classification of Crystals and Molecules according to their Vectorial Fields by P. P. von Weimarn; Surface and Catalysis by E. F. Armstrong; Contact Catalysis by H. S. Taylor; Adsorption by Silica Gel, Theory and Applications by E. B. Miller; Colloid Factors in Water Supply by W. D. Turner and D. D. Jackson; Crushing and Fine Grinding of Quartz by Louis Navias; Colloid Mills and Comminution Chemistry by August Chwala; Suspensoids and their Electrical Precipitation by W. W. Strong; The Super-Centrifuge in Industry by E. M. James; Notes on Filtration with Special References to Metafiltration by J. A. Pickard; the Flotation Process by G. H. Buchanan; Chemical Warfare by Jerome Alexander; Colloid Chemistry and Geology by R. E. Liesegang; Colloidal Minerals by Cornelius Doelter; Colloids in Glass by Alexander Silverman; Some Colloidal Properties of Sodium Silicate Solutions by William Stericker; Porcelain and Allied Ceramic Bodies by Louis Navias; Ceramic Refractories as Disperse Systems by E. W. Washburn; The Colloidal Nature and Properties of Cements and Mortars by A. B. Searle; The Colloidal State in Metals and Alloys by Jerome Alexander; Colloidal Conditions in Metal Crystals by W. Guertler; Colloidal Systems in Metallography by Carl Benedicks; The Well-known Five Structures in Steel by Kôtarô Honda; The Rôle of Surface Energy on the Equilibria of Iron and Iron Carbide by Yap, Chu-phay; The Properties of Thin Films on Metals by U. R. Evans; The Colloids and the Corrosion of Iron by J. N. Friend; Colloid Chemistry and Petroleum by A. E. Dunstan; Colloid Chemistry of Petroleum by J. C. Morrell and Gustav Egloff; Colloid Chemistry and Petroleum by L. Gurwitsch; The Free Carbon of Coal Tar by J. M. Weiss and C. R. Downs; Asphalt by E. J. Nellensteyn; Deflocculated Graphite by E. G. Acheson; Colloid Fuel by L. W. Bates; Soil Colloids by J. di Gleria and Fr. Zucker; The Colloidal Chemistry of the Soil by Richard Bradfield; Rapid Colloidal and

Mechanical Analysis of Soils by G. J. Bouyoucos and M. M. McCool; The Colloid Chemistry of Wheat, Wheat Flour, and Wheat Flour Products by R. A. Gortner.

"That thin films are very much stronger than an adhesive *en masse* is established by Crow's results for soft solder and our much more striking instance of a wax-free shellac. Joints made with this shellac, which is fairly soft and quite pliable, actually withstood a pull of nearly 4000 lb. per sq. in. when a thin film was used between nickel surfaces. We have found that optically plane surfaces prepared at the National Physical Laboratory yield stronger joints than those which have not been prepared with such precision. An examination of the broken joint served to show how exceedingly thin was the film between those highly polished surfaces. The amount of adhesive attached to the metal was just sufficient to dim the lustre. Incidentally the results of the tests carried out with a shellac-creosote cement between optically plane surfaces of mild-steel and nickel prove beyond doubt that surface roughness plays but a negligible part in determining the strength of a 'specific' joint for here we have the smoothest possible surfaces yielding stronger joints than those prepared in the ordinary way and which are therefore comparatively very rough, "p. 22.

"Krishnamurti has found for samples of sugar, benzene, and naphthalene charcoals and carbon obtained by charring ash-free gelatin with molten sodium, together with colloidal graphite prepared by exploding graphite acid in a vacuum, that all showed the small angle scattering in a marked manner. The patterns showed two rings in addition to the central scattering, the first and prominent ring corresponding to the (002) reflection of graphite, having a spacing of about 3.8 A.U. as compared to 3.4 A.U. of graphite. The outer ring was fainter and broader and showed a spacing of 2.12 A.U. comparable to the (111) spacing of graphite (2.06 A.U.). The observations accord with the idea that in the amorphous state the carbon atoms join together in clusters, forming highly anisotropic units, essentially two dimensional, the thickness being about 1/3 the length or breadth. Assuming that the central scattering is due to the dimensions in the plane of the particle, and the first ring to its thickness, a rough calculation gives about 60 atoms of carbon per unit. This picture of the carbon particle agrees with chemical evidence, mainly its oxidation to mellitic acid and adsorptive properties," p. 33.

"Following the discovery of Krishnamurti that diffraction patterns of aqueous solutions of cane sugar, levulose and glucose were distinguished by intense scattering at small angles due to the dissolved molecules, it was then possible to undertake the study of colloidal solutions for which the state of molecular aggregation has been the subject of much speculation. The molecular weight of dextrin calculated from the extent of "amorphous" scattering by means of the Bragg formula $n\lambda = 2d \sin \theta$ comes out 600, and for gelatin, 3,000, which are not improbable values. The solution of sodium oleate produced a ring due to the presence of big groups or micelles of sodium oleate in the solution. The extent of the gaseous scattering gave the dimension for the sodium oleate molecule, agreeing with that calculated from molecular weight and density. An excess of scattering directly adjoining the central spot, is due to big groups of ionic micelles described by McBain. Aqueous solutions of starch, tannic acid and gum arabic showed a further scattering at small angles to the primary beam, due to the dissolved molecules or micelles. The molecular weights calculated from the extents of the coronas were 6,200, 3,134, and 2,810, respectively. Thus, a starch molecule contains about 10 dextrin molecules united together, and a tannin micelle contains 10 simple molecules of the formula $C_{14}H_{10}O_9$. The great importance of these studies is at once apparent, when it is considered that extremely valuable information should be obtained from biological fluids including blood, filtrable virus, etc. In all these cases of amorphous solids, liquids and solutions, the X-ray patterns are characteristic in showing the presence of one or more diffraction bands, even though these may be ill defined. The purely amorphous scattering where no maxima are present, evidently can exist only in the case of ideal gases. All of these newer investigations are in agreement with the contention by the writer that such a material as amorphous carbon represents an intermediate state designated as a paracrystalline, through which the atoms of carbon have to pass before obtaining the orderly arrangement underlying the graphite structure," p. 34.

"There has been a very considerable disagreement concerning the structures of gutta percha and balata which are like rubber, polymers of isoprene. The discrepancies have at last been explained in the work of Kopff and von Susich and of Stillwell and Clark. These two substances produce diffraction patterns different from rubber, but probably like each other. There are two modifications, the α which is stable below 60°C. and β produced by heating above 60°, giving different patterns in the unstretched state. The β-modification also produces a fiber pattern, since the specimens must be warmed before stretching. Stillwell and Clark have found balata in ordinary commercial form to differ from ordinary gutta percha, in the same way that von Susich's β-modification differs from β-gutta percha," p. 37.

"A plausible mechanism for muscular action can be deduced in terms of inner molecular forces. Rubber contracts because of double bonds in the long hydrocarbon chains which cause a spring-like coiling. In muscle protein there are many free basic and acid groups in the chains, since glutaminic acid and arginine and lysine may be derived. At the isoelectric point COO^- and NH_3^+ ions may attract and pull the chain into a close spiral," p. 39.

"If wetting be defined as 'that phenomenon which occurs when a solid phase and a liquid phase come in contact in any manner, so as to form a solid-liquid interface,' the ground for controversy relative to wetting and non-wetting has been removed. There remains only the question of degree of wetting of the solid by the liquid. If it be further specified that degree of wetting means the amount of change in free surface energy which occurs (or the work done by the system) when the solid and liquid are brought together, all confusion can be avoided," p. 41.

"Carbon pigments are used as a *filler for rubber*. Carbon gives an exceptionally high adhesion against the organic constituents of the rubber; this is desirable as it results in a product of high elasticity and good wearing qualities. Over one hundred million pounds of carbon black are used per year in the rubber industry alone. Large quantities of carbon pigments are used also in *printing inks*, in *stove polishes*, and in *shoe polishes*. In each of these preparations the liquids used must give a high degree of wetting with the pigment. In printing inks the liquid medium must possess a fairly low surface tension in order to give a smooth flow over the surface with a minimum tendency for the ink to pull up into drops; on the other hand 'spreading wetting' (the magnitude of which is increased as surface tension of liquid is decreased) against the paper cannot be too high, otherwise a sharp imprint will not be obtained," p. 54.

"Three different groups of facts lead, therefore, to the assumption that gelatine has a sponge or net-like structure," p. 86. "A system possessing the high elasticity of rubber must have the following structure: (1) The *primary* structure elements of such a system must possess the form of spirally curled fibrils; (2) the interfibril dispersion medium must be extremely viscous (plastic) and permit the fibrils, after the stretching out of the system, to become curled when the system has been released from tension," p. 96.

"It is the specific nature of the catalyst which determines what the chemical change shall be. More closely studied from this point of view has been the reaction of carbon monoxide with one, two or three molecules of hydrogen, producing formaldehyde, methyl alcohol or methane respectively. Any desired one of these three products can be made with the practical exclusion of the others, provided that a suitable temperature and catalyst is selected. A copper catalyst at 300° to 400°C. favors the formation of formaldehyde; to produce methyl alcohol a reduced basic zinc chromate is necessary at 300° to 350°C., whilst for methane the best catalyst is nickel at 150° to 200°C. The reactions are carried out at fairly high pressures," p. 103.

"The linearity of the time-hydrogen-adsorption curve in cases of hydrogenation in liquid media is held to be evidence of interaction of the organic compound rather than the hydrogen with nickel, because the rate of absorption varies during the course of hydrogenation of many unsaturated substances containing two ethylenic linkages at or near the point at which the material becomes semi-hydrogenated, and chemical analysis has shown in such cases that the reduction has been 'selective,' that is the two centres of unsaturation are reduced in number to one before any proportion of the singly unsaturated product is com-

pletely hydrogenated. Consequently, the slope of the time-absorption line is definitely correlated with the organic compound present. It is desirable to emphasize this most striking feature whilst at the same time bearing in mind that hydrogen undoubtedly also becomes associated with the nickel," p. 105.

"The extent of the surface which is active varies with the nature of the reaction catalyzed. There is unequivocal evidence that, in certain reactions, every atom in the surface is active. In others the evidence is equally definite that only a small fraction of the surface is active. In the former case the reaction is relatively insensitive to poisons, in the latter case extremely sensitive. Hence arises the possibility of progressive poisoning in which, on a given catalyst, different reactions are successively stopped by increasing amount of poison. The study by Vavon and Huson of a colloidal platinum on which the hydrogenation of propyl ketone, piperonal, and nitrobenzene were successively suppressed by addition of increasing quantities of sulfide poisons is a good example of such behavior," p. 108.

"When we turn from elementary catalysts such as the metals to catalysts composed of compound materials with ionic lattices such as oxides, halides, sulfates, etc., the surfaces in question contain an additional factor of variability. Such ionic lattices may be regarded as dual catalysts, the surface being composed of metal ion and negative ion. To each type of ion may be ascribed a definite and specific catalytic activity. Examination of the catalytic behavior of the oxides suggests that, on the metal ion, processes of hydrogenation and dehydrogenation occur, whereas, on the oxide ion, the processes are essentially hydration and dehydration. With a given process, the extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors (extent of adsorption, frequency of ions in the surface and catalytic activity) will be determined by the degree of saturation of the lattice ions, and by the extent to which the ions are already covered by poisons (salts, water, ammonia, etc.). With this concept, the variation in dehydration-dehydrogenation ratio of various oxide catalysts in, for example, formic acid decomposition

$$HCOOH = H_2 + CO_2$$
$$HCOOH = H_2O + CO$$

and ethyl alcohol decomposition

$$C_2H_5OH = CH_2CHO + H_2$$
$$C_2H_5OH = C_2H_4 + H_2O,$$
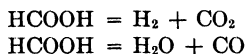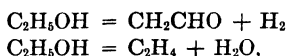
receives a more satisfactory interpretation than has hitherto been suggested for such reactions," p. 109.

"Probably the most important application of silica gel so far developed commercially is in the so-called contact sulfuric acid process. As a carrier for platinum it is ideal. It is chemically inert to sulfuric acid at high temperatures, stands up under continuous high temperature conditions, is resistant to mechanical action and offers an enormous surface upon which to distribute the platinum. Besides possessing these qualities silica gel mass has also proven insensitive to the usual negative effect of arsenic poisoning," p. 133.

"Micro-organisms often give trouble in reservoirs which at certain seasons may become literally hotbeds for the growth of various types of microscopic forms, which will contribute colloidal impurities to the water. The combined influences of warmth, sunlight, and quiet are all contributing factors which may sometimes be very difficult to alter. In certain regions reservoirs must be covered wherever possible to exclude sunlight, and thus inhibit microscopic growths. In Bermuda, for instance, where the climate is temperate, but the sun is hot, raw water cannot be stored in the sunlight for even forty-eight hours without becoming green from the prolific growth of chlorophyceae. All storage tanks in the region are, therefore, constructed with covers to keep out the light," p. 137.

"Red water occasionally gives trouble in certain water pipes, particularly, the system within private properties, and especially the hot water systems. This rusty discoloration is due to colloidal ferric iron in the water and is usually traceable to the effect of dissolved air or oxygen on the walls of the iron pipe. The effect is noticed more frequently with soft water and obviously more so with hot water. In New York City the water is so soft that

incrustation in water heaters takes place very slowly, or not at all. Here it is, therefore, not uncommon to find the water in hot water pipe lines running brick red from the iron contamination originating within the heater system," p. 138.

"Reaction of the negative colloidal color with the positive nucleus of the coagulating agent (copperas or alum) gives flocculation precipitation and decolorization, but as pointed out by Whipple colored waters having the negative property increased by addition of CO_2 can be better decolorized by alum coagulation. This is in conformity with the experience of Jackson, who found that the highly colored water in the Everglades region of Florida could be successfully decolorized, first, by adjustment of the hydrogen ion concentration by addition of so active an agent as sulfur dioxide, followed by the customary addition of alum coagulant," p. 150.

"The traces of certain impurities which may give trouble are sometimes astonishingly small. This is well illustrated by an experience of the large rayon plant near Buffalo. Here it was definitely established that the discoloration in the top skeins of piles of fiber through which they were running wash water was due to a trace of copper in the water which gave trouble in concentrations as low as one part in 40,000,000," p. 153.

"Where no solvents are present, from solid non-gels there are formed only turbidities, provided that there are used as peptizers only substances which are polar and relatively slightly active. Solvates, on the other hand, form sols, but require as peptizers very active molecules having the power to form true compounds which can fasten themselves to the particle surface. The slightly active polar substances which serve as peptizers for solid non-gels, are incapable of orienting themselves on solvates," p. 188.

"The sedimentation of *Bacillus acidophilus* from broth culture furnishes an interesting example of the ability of the centrifuge to remove finely divided solids. The bacilli, which vary in length from 1μ to 3μ, and have a diameter of approximately 0.5μ are formed in the broth culture under carefully controlled conditions. When the concentration of the bacilli has reached fifteen hundred million per cubic centimeter, the broth is ready for centrifugal treatment. It is fed through a battery of super-centrifuges at the extremely low rate of 10 gallons per hour, and the effluent, whose bacterial count has been reduced to twenty-five million per cubic centimeter is wasted. When the centrifugal rotors are opened, the bacilli are found adhering to the wall of the bowl in a putty-like mass. From this form they are worked up into a special preparation, providing extremely high bacterial concentration," p. 210.

The tonnage of ore treated in the United States alone by the flotation process amounted "in 1929 to sixty million tons. At one metallurgical operation alone forty thousand tons of ore are treated daily," p. 225.

"The so-called 'Sea of Darkness' in the Atlantic Ocean between Cape Verde Island and the Canaries, probably owes its origin to dust storms from the Sahara Desert, especially between January and April. According to Hellman and Meimardus, a cyclonic storm central over Tunis about March 8-10, 1901, deposited about 150 million tons of dust on the African coast, and further great but incalculable amounts in the Mediterranean Sea. So high did the dust rise, that about one-third of the 1,800,00 tons deposited in Europe fell north of the Alps. E. R. Miller and A. W. Winchell traced a storm of dust-colored snow from Dubuque, Ia., to Chelsea, Vt., over an area of 100,000 square miles; the dust, apparently originating in the deserts of Arizona and New Mexico, must have been carried at high altitudes for over 1,000 miles before being brought down. The daily papers reported on December 19th, 1930, that a terrific storm swept over northern Algeria following a serious seven months drought; and on December 22nd the papers reported that a terrible fog (visibility 3 feet) had paralyzed London. Just prior to this (Nov. 27, 1930) a terrific sand-storm and hurricane blew over French Morocco, carrying a heavy deposit of yellow sand to the streets and foliage of Barcelona the next night. On the morning of Nov. 29th, a 'Mud-rain' fell in Paris, along the English Channel and the coast of Brittany. [See Jerome Alexander: Science, **63**, 96 (1931)]," p. 260.

"The ascidian *Phallusia* has a vanadium-containing blood; manganese occurs in mussels; copper in most molluscs," p. 275.

"As a matter of fact, comparatively little is known about the chemical reactions of the sodium silicates in aqueous solutions. . . . If results are reported without specifying the silicate, many questions remain. As an example of the possible contradictions, the reaction with calcium carbonate studied by Carter, may be cited. He found that $Na_2O.2SiO_2$ would react with $CaCO_3$; but that neither $Na_2O.1.6SiO_2$ nor $Na_2O.3.3SiO_2$ showed any evidence of reacting within a period of a week," p. 295.

"Refractory materials are known to have extraordinarily high latent heats of fusion and consequently also very high heats of sublimation," p. 352. It seems to the reviewer that the vapor pressure should increase rapidly with the temperature if the heat of sublimation is very high and that consequently refractories should sublime at relatively low temperatures, in which case they would not be refractories.

"It seems to the present writer [Alexander] that there is no good reason to doubt the existence of Fe_3C, especially when the steel is semi-solid or solid, for there exists a condition of kinetic or dynamic equilibrium in which this compound is being continually formed and broken up, so that while a certain percent of free carbon atoms may exist at any one moment, there is probably an enormously larger percentage of Fe_3C. Viewed from the standpoint of a kinetic equilibrium, all difficulty regarding the diffusion of Fe_3C disappear," p. 429.

"Cold bauxite, which has been ignited and cooled in a vacuum desiccator was found to have lost its power of adsorbing sulfur derivatives from kerosene. When freshly heated (to $200°C.$) its activity in this direction was regained. Heat appears to be evolved during active adsorption, thus a $20°C.$ rise in temperature was observed during the passage of 100 cc. of kerosene through 50 grams of bauxite," p. 494.

"It is estimated that in 1930 three hundred million barrels of the world's total crude oil production was produced in emulsion form, and required some form of treatment before it could be marketed," p. 504.

"From the economic point of view colloidal fuel possesses many advantages over fuel oil or coal alone. First, the fire hazard of colloidal fuel is less than that of oil or coal. The specific gravity of a composite using over about 15 percent of coal is greater than unity. If on fire, the flames may be quenched in and by water, and, in storage, fire may be prevented by a water seal. This fact is of cardinal importance as other liquid fuels are lighter than water and cannot be so safeguarded. Trials of a water seal have shown that certain grades of the fuel may be so stored for even a year without jeopardizing their operative character. Sprinkler systems of fire protection do not lose their utility as they do in plants using oil fuel. The insurance advantage and increased safety of ships and plants due to this fireproofing capacity is obvious," p. 557.

"The great interest practical soil chemists have shown in base exchange phenomena in the last few years is due largely to the fact that an understanding of these reactions promises to throw much light on several of the most important problems in soil management. Such studies as indicated above have served to greatly clarify some of the problems connected with the acid soils of the humid region. The proportion of exchangeable hydrogen in the colloidal fraction, or the "degree of unsaturation with bases" as it is commonly called, is one of the best measures we have of the degree of acidity of a soil," p. 587.

Wilder D. Bancroft

Essentials of Quantitative Chemical Analysis. *By Wilfred W. Scott. 23 × 15 cm; pp. viii + 219. Easton: The Chemical Publishing Co., 1931. Price: $2.75.* This is a new and enlarged edition of Scott's "Inorganic Quantitative Chemical Analysis," 1926. The text contains a comprehensive list of experiments of general educational value for students in introductory quantitative analysis. The arrangement is much the same as the previous addition although several procedures have been entirely rewritten and a number of new methods have been introduced.

The notes and theoretical discussions accompanying the experiments have been increased over those of the previous edition. Numerous references for outside reading and a list of study questions in the addenda of the text are also included.

M. L. Nichols.

Handbuch der allgemeinen Chemie. *Edited by Paul Walden and Carl Drucker. Vol. VIII. Part I. Elektromotorische Kräfte. By R. Kremann and Robert Müller. 25 × 17 cm: pp. xvi + 891. Leipzig: Akademische Verlagsgesellschaft, 1930. Price: 81 marks; bound, 85 marks.* This volume covers the whole field of electromotive forces, not differentiating between aqueous and non-aqueous solutions. The chapters are entitled: introduction; measurements of electromotive forces; conversion of chemical energy into electrical energy by means of galvanic [voltaic] cells and the temperature coefficient of such cells; Nernst's osmotic theory of the galvanic production of current; solution cells; concentration cells; amalgam cells; galvanic cells of the Daniell type; effect of pressure on reversible galvanic cells—gravity cells; determination of single potential differences at phase boundaries in galvanic cells; potential differences at other phase boundaries than those between metals and solutions; electrolytic solution pressure; single potential in cells; potentials of alloys; oxidation-reduction cells; normal potentials of electrode reactions; formation of metals and alloys by precipitation.

"The current in a cell of the Daniell type is due to the fact that the less noble metal (zinc) dissolves, sending positive ions into the solution, and becoming charged negatively itself, while simultaneously equivalent amounts of the ions of the nobler metal (copper) are precipitated on the copper electrode, thereby charging this positively. The equalization of the potential differences takes place in the external circuit with production of electrical work," p. 4.

On p. 13 the authors say that Helmholtz later developed independently the Gibbs formula. This is not true at all. Gibbs developed a theory to show that the electrical energy of a reversible cell is not necessarily equal to the heat of reaction. When Helmholtz deduced the equation for the relation between electromotive force, temperature coefficient, and heat effect, Gibbs showed that the same equation could be deduced from the Gibbs theory. Gibbs did not deduce it and there is nothing to show that he would have deduced it if Helmholtz had not done so.

On p. 20 and elsewhere throughout the book the authors write the formula of mercurous chloride as HgCl, although they cite Ogg's work, p. 99, showing that the mercury ion is Hg_2. Eight pages are given, p. 38, to the application of Nernst's heat theorem to voltaic cells. A good compilation is given, p. 111, of the data on concentration cells in non-aqueous solvents. On p. 132 there is a warning as to errors in electrometric titration caused by adsorption. The authors do not seem to know, p. 136, that there is always retrograde solubility with rising temperature whenever a binary compound is stable at its melting-point. It is difficult to tell, p. 144, what the authors' attitude is towards Spencer's measurements on amalgam cells. On p. 213 is given the deduction by Gans of the effect of pressure on electromotive force when the transference number varies.

"Arrhenius showed that air can act as an electrolyte. If one brings a zinc wire and a platinum wire into a tube pumped out to a pressure of 0.1-2.0 cm, and if one makes the air a conductor by means of cathode rays, a current is obtained between the metals flowing in the direction that it would if the metals were dipped in air; the electromotive force averaged about 0.86 volt," p. 221.

It is recognized, p. 248, that the maximum-surface-tension method does not give the true single-potential difference because of adsorption; but nobody seems to have determined the absolute maximum-surface-tension of mercury in any of these solutions. If the value in sulphate solutions were very close to the true surface tension, the error would be very small. If it were very large, the error would be correspondingly large and there might even be an agreement between this method and that of Billiter. The theory of Frunkin, p. 256, does not appear to come out with anything positive. The authors throw out Billiter's work, p. 276, because the potential difference of silver against a solution is a function of other things besides silver ions; but the potential difference of a hydrogen electrode is a function of chloride, bromide, and iodide ions.

There is a very good account of Haber's work on phase boundary potentials, p. 281; of membrane cells, p. 291; and of the Donnan equilibrium, p. 299. On the other hand, they quote with approval, p. 325, Luther's statement that the potential difference between a

metal and a saturated solution of a salt of the metal is independent of the nature of the solvent. The discussion of the change of the solution pressure with the solvent, p. 326, is rather exceptionally poor. From a table for heats of ionization of metals, p. 351, the authors draw the conclusion that all metals which form ions readily have positive heats of ionization, while others have negative heats of ionization. Tin seems to be an exception.

In the discussion of the hydrogen-lead peroxide cell, p. 362, the authors point out that a much larger current can be drawn without polarization with palladium electrodes than with platinum electrodes. Apparently the rate of conversion of molecular into atomic hydrogen is much lower with platinum than with palladium. Also the oxygen polarization of the platinum electrode poisons the latter. Addition of colloidal platinum to a solution, p. 439, makes it possible to use smooth platinum electrodes. Strong poisons for metals, p. 441, are naphthoquinoline, strychnine, brucine, narcotine, and quinine. Less strong are nicotine, veratrine, cocaine, and cinchonine.

Amalgamated aluminum in $N/10$ $AlCl_3$ gives a potential difference of 1.66 volts against the normal calomel electrode. Since aluminum cannot be precipitated from an aqueous solution, the aluminum electrode is theoretically irreversible and its electromotive force is consequently not a function of the concentration of aluminum ions. This is not true for a fused mixture of aluminum and potassium bromides, p. 476. Aluminum dissolved much more rapidly in hydrochloric acid than in equimolecular hydrobromic or hydriodic acid, p. 477. The authors draw the apparently unwarranted conclusion that the rate of attack is proportional to the concentration of the undissociated acid.

Since iron takes up hydrogen readily and also oxidizes readily in water, its potential is hard to determine. The authors consider $\epsilon_h = -0.46$ as representing the equilibrium potential, p. 541. The intermittent action of acids on chromium is believed to be due to iron in the metal, p. 557. With pure iron in chromic acid, periodic fluctuations of 0.4 volts can be obtained, 558.

While sulphur may form quadrivalent cations, as indicated by the conductivity of liquid sulphur dioxide, it is not legitimate to postulate this from the fact that sulphur is set free at the cathode in the electrolysis of concentrated sulphuric acid, p. 573. That sulphur comes from the interaction of sulphurous acid with hydrogen sulphide.

If one superposes an alternating current on a direct current one can get evolution of hydrogen and oxygen below the point of reversible equilibrium for the oxyhydrogen gas cell. On increasing the alternating current relatively to the direct current, Grube and Dulk found a break in N NaOH at 1.24-1.26 volts which is very close to the theoretical value of 1.237 volts, p. 589. The experiments of Tartar and Wellmann show that soluble substances. possibly hydrogen peroxide, are also a factor, p. 590.

If platinum is precipitated electrolytically on porous charcoal, a film is obtained through which hydrogen passes with great ease and permits a current of twenty milliamperes per square centimeter, p. 613. Butler, Hugh and Hey find that constant potentials as non-attackable electrodes are reached by platinum, palladium, iridium, osmium, gold, rhodium, and ruthenium in about an hour, while molybdenum, tungsten, nickel, silver, and mercury are not certain to give constant potentials at all, p. 663.

The treatment of the effect of hydrogen ions on the potential difference due to oxidizing and reducing agents is perfunctory and unsatisfactory, p. 669.

There are a number of interesting facts on p. 697. A ferrous-ferric salt solution can be prepared which will precipitate silver and not copper. Addition of sodium fluoride causes the precipitation of metallic copper. An alkaline stannite solution precipitates metallic cadmium. There is a distinct over-voltage for hydrogen in vanadous chloride solutions, which can be overcome by platinum metal.

Sixteen pages are given to the quinhydrone electrode, p. 713. It is not clear why cane sugar should affect the readings but it does, p. 723. On pp. 786-790 there is a fairly complete table of electromotive force measurements depending on oxidation or reduction.

The book is a marvellously good one as a collection of facts. The authors are worshippers of the letter, however, and no one will turn to them for inspiration.

Wilder D. Bancroft

CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE—I

BY C. J. ENGELDER AND L. E. MILLER*‡

This paper is a record of the results of experiments carried out on the catalytic oxidation of carbon monoxide by titania and mixtures of titania with various metallic oxides. The investigation had for its main purpose the study of a number of metallic oxides with titania, with the hope of finding a mixture that would be catalytically active toward the oxidation of carbon monoxide to carbon dioxide at room temperatures and in the presence of water vapor.

Titania has been a favorite catalyst in this laboratory for a number of years. Rudisill and Engelder[1] investigated various factors influencing the catalytic activity of titania in the decomposition of ethyl alcohol. Wescott and Engelder[2] studied the catalytic decomposition of formic acid over titania. On the basis of its activity towards ethyl alcohol and formic acid titania merited special consideration in the reaction, $2CO + O_2 \rightarrow 2CO_2$, in the present research.

Much of the previous work upon the catalytic oxidation of carbon monoxide has been centered upon the study of manganese dioxide, cupric oxide, and mixtures of these oxides. The story of the development of hopcalite for the oxidation of carbon monoxide is well known. Lamb, Bray, and Frazer and their associates[3] conducted most of the investigations which culminated in the production of this well known catalyst. Much of the later work on the catalytic oxidation of carbon monoxide upon the various factors influencing the catalytic activity of hopcalite and its constituent oxides, has been reported by these same investigators.

Bone and his co-workers[4] studied the combustion of carbon monoxide with oxygen over nickel, copper, and their oxides. Other interesting contributions on the subject of carbon monoxide oxidation have been made by Benton and Williams[5] who studied the catalytic oxidation of carbon monoxide in con-

[1] W. A. Rudisill and C. J. Engelder: Catalytic Activation of Titania, J. Phys. Chem., 30, 106-113 (1926).

[2] B. B. Wescott and C. J. Engelder: The Catalytic Decomposition of Formic Acid, J. Phys. Chem., 30, 476-479 (1926).

[3] A. B. Lamb, W. C. Bray and J. C. W. Frazer: The Removal of Carbon Monoxide from the Air, J. Ind. Eng. Chem., 12, 213-221 (1920).

[4] W. A. Bone and G. W. Andrew: Studies in Catalytic Combustion. II. The Union of Carbon Monoxide and Oxygen in Contact with Nickel, Copper, and their Oxides, Proc. Roy. Soc., 110-A, 16-34 (1926).

[5] A. F. Benton and T. L. Williams: The Catalytic Oxidation of Carbon Monoxide in Contact with Quartz Glass, J. Phys. Chem., 30, 1487-1496 (1926).

tact with quartz glass. Taylor and Jones[6] made observations on the velocity of carbon monoxide-oxygen combination over copper and copper oxide.

Experimental Method

For the purpose of testing the activity of the various catalysts whose action was studied in this investigation, a definite method was adopted. It consisted in passing carbon monoxide-air mixtures over a sample of the finely ground catalysts contained in the tube of an electrically heated furnace. Analyses were made of the influent and effluent gases for carbon monoxide and carbon dioxide. In all cases one gram of the catalyst was used. The gas mixture which usually contained 10-12 per cent carbon monoxide was maintained at a uniform rate of flow of 50-60 cc. per minute. The duration of a test was usually two hours.

Apparatus. The apparatus for the experimental work consisted of an electrically heated tube furnace as described by Nelson and Engelder[7] in their experiments on the thermal decomposition of formic acid. The temperature was automatically regulated by a Leeds and Northrup temperature controller. The catalyst was contained in a porcelain boat placed in the center of the furnace. The carbon monoxide-air mixture which was contained in a 20-liter carboy was forced over the catalyst by displacing the gas mixture with water from an aspirating bottle. The effluent gases were collected over salt water in a second 20-liter carboy.

The carbon monoxide was prepared by dropping formic acid on hot sulfuric acid. It was freed from sulfur trioxide, sulfur dioxide, carbon dioxide, and formic acid fumes by passing it through a canister containing activated charcoal and soda-lime.

Analysis of Gas Mixtures. The analysis of the gas mixtures was made in the apparatus of Hempel. Carbon dioxide was absorbed in a fifty per cent KOH solution. Oxygen was taken up in alkaline pyrogallol and carbon monoxide in acid cuprous chloride solution.

Preparation of the Catalysts. In order to promote uniformity and to avoid any uncertainty due to the manner of preparation, the catalysts were prepared according to a uniform plan. In general the titania catalysts were prepared according to the method described by Rudisill and Engelder[8] in their experiments on the catalytic activation of titania. Titanium hydroxide was precipitated from a solution of titanium potassium oxalate by ammonium hydroxide. The precipitate was dissolved in dilute sulfuric acid and reprecipitated again with ammonium hydroxide. The precipitate was washed several times by decantation until free from sulfates. It was filtered by suction, and then dried at 150°C. in a drying oven. In the case of titania

[6] H. S. Taylor and H. A. Jones: The Reduction of Copper Oxide by Carbon Monoxide and the Catalytic Oxidation of Carbon Monoxide in presence of Copper and Copper Oxide, J. Phys. Chem., **27**, 623-651 (1923).

[7] W. L. Nelson and C. J. Engelder: The Thermal Decomposition of Formic Acid, J. Phys. Chem., **30**, 470-476 (1926).

[8] W. A. Rudisill and C. J. Engelder: loc. cit.

with the various metallic oxides the hydroxides were precipitated simultaneously from the solutions which would yield the oxides in the proportions by weight desired. So far as was possible the C.P. nitrate salts were used. In certain instances the sulfates were employed for the starting material.

The mixed oxide catalysts were given the same treatment as the titania catalysts. They were dried for about twelve hours and activated by ignition at a temperature of 300°C. for two hours preceding their use.

Experiments with Titania

In Table I are given the results of some representative experiments with titania. These will illustrate the activity of titania toward the catalytic oxidation of carbon monoxide. Titania was not found to be active at temperatures much below 300°C. Experiments carried out at 150°C. showed that with the best titania catalysts only 10-12 per cent of the carbon monoxide was oxidized. From an inspection of the table it may be observed that the titania catalysts were more active at the end of a four-hour run than at the end of a two-hour run. Experiment 2 in the table illustrates the unlimited activity of the titania catalysts.

TABLE I

Experiments with Titania

All catalysts received the same preliminary treatment. Temperature of ignition, 300°C. One gram of catalyst used. Rate of flow, 50-60 cc. per minute. Duration of run, two hours. CO-air mixture saturated with H_2O. CO, 10-12 per cent. Temperature of furnace, 300°C.

Experiment	Percentage of Oxidation at 300°C.				
	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
1	70.4	75.2	—	—	—
2	74.5	84.9	88.2	85.9	86.3
3	58.9	67.7	—	—	—
4	74.1	79.6	—	—	—
5	55.3	71.6	—	—	—

The difficulty in obtaining identical results for catalysts prepared according to a uniform plan illustrates what differences there must be in the catalytic surfaces of different samples of catalysts from the same preparation.

In order to study the effect of the method of preparation of the titania catalysts on their catalytic activities, a titania catalyst was prepared by employing potassium hydroxide for the precipitant. The various steps in the method of preparation with the exception of the precipitant were exactly the same as that described for the titania catalysts prepared by precipitation with ammonium hydroxide. The results from the two following experiments (Table II) show in general how the titania catalysts prepared by ammonium hydroxide were the more active.

<div align="center">TABLE II</div>

Experiments to show the Activity of Titania prepared by Different Precipitants

Rate of flow, two liters per hour. One gram of catalyst used. Duration of run, two hours. CO-air mixture, dry. CO, 10-12 per cent.

Catalyst	Percentage of Oxidation at 300°C.	
	2 hrs.	4 hrs.
TiO_2 (precipitated with NH_4OH)	92.5	95.8
TiO_2 (precipitated with KOH)	76.9	71.8

While considerable experimental work was done in order to develop a uniform method of procedure, it was observed that such fumes as H_2S and vapors from gasoline, naphthas, and oils had a very marked detrimental effect upon the activity of the catalysts when they were present in the same laboratory in which the catalysts were being prepared. A laboratory remote from any of these disturbing factors was finally selected for the preparation of the catalysts.

Experiments with Titania and Various Metallic Oxides

Although titania in itself proved to be a very good catalyst for the oxidation of carbon monoxide at 300°C. and very poor at a temperature of 150°C., it was thought that the addition of other oxides to titania might have a promoting action. Accordingly preliminary experiments were made with mixed catalysts of 99 per cent titania and 1 per cent of various oxides. The following oxides were tried: UO_2, Fe_2O_3, NiO, Cr_2O_3, Co_2O_3, CeO_2, CuO, SnO_2, MnO_2, ZnO, ThO_2, Bi_2O_3, HgO, Al_2O_3, Ag_2O, MgO, and CdO. From this list the first seven were selected for further study. Experiments were made at 300°C. and 150°C. with mixtures from 1 per cent up to 80 per cent with titania. The results of this extended study are recorded in Tables III and IV.

The best catalysts were obtained from mixtures of the metallic oxides with titania approximating a 50:50 ratio of mixed oxides. The results for ceria, which was only moderately active at 300°C., with titania illustrate the superiority of mixtures in this proportion as may be observed from Table III. In Table IV the combination of titania with ferric oxide shows again the superior activity of mixtures in this ratio. The results for mixtures of titania with nickel oxide and titania with copper oxide in Tables III and IV show that very active catalysts were obtained at these temperatures. Experiments at lower temperatures showed that catalysts in the ratio of 60 per cent titania and 40 per cent copper oxide were more active than when combined in any other proportion.

Titania and ferric oxide are both fairly active catalysts for the oxidation of carbon monoxide at 300°C. Mixtures of titania with ferric oxide produced catalysts that were quite active at 150°C., a temperature much below that

TABLE III

Experiments with Mixtures of Titania and Various Metallic Oxides at 300°C.

Oxide used — Percentage of Metallic Oxides present with Titania

Percentage of Oxidation at 300°C.

Oxide used	1	5	10	20	30	40	50	60	70	80	100
UO₂	13.4	74.8	59.3	—	17.4	—	17.2	—	—	0.0	0.0
Fe₂O₃	43.4	59.4	86.5	98.4	97.8	100.0	100.0	100.0	100.0	100.0	98.4
NiO	58.1	—	61.6	89.5	92.3	96.4	100.0	100.0	100.0	100.0	98.3
Cr₂O₃	6.1	—	—	—	—	100.0	—	93.4	—	—	92.1
CeO₂	43.2	—	—	—	—	100.0	—	100.0	—	—	37.3
CuO	100.0	—	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	93.3

TABLE IV

Experiments with Mixtures of Titania and Various Metallic Oxides at 150°C.

Oxide Used — Percentage of Metallic Oxides present with Titania

Percentage of Oxidation at 150°C.

Oxide Used	1	5	10	20	30	40	50	60	70	80	100
UO₂	—	10.0	0.0	—	0.0	—	0.0	—	—	—	—
Fe₂O₃	0.0	5.8	6.0	7.7	36.5	51.6	78.8	86.4	81.1	10.6	45.6
NiO	0.0	—	0.0	0.0	12.5	9.5	90.9	100.0	100.0	100.0	91.9
Cr₂O₃	0.0	—	—	—	—	0.0	—	—	—	—	·10.7
Co₂O₃	—	—	0.0	—	—	100.0	—	100.0	—	—	100.0
CeO₂	0.0	—	—	—	—	24.2	—	25.2	—	—	0.0
CuO	53.1	—	100.0	100.0	91.8	100.0	100.0	100.0	—	100.0	78.3

at which these oxides are catalytically active. Pease and Taylor[9] gave the term "co-activation" for such cases of increase in the catalytic activity of mixed oxides as is shown by the mixture of titania with ferric oxide.

Bone and Andrew[10] investigated the action of nickel and nickel oxide in the catalytic combustion of carbon monoxide. They found that at 150°C. nickel oxide became fairly active catalytically without any appreciable reduction of the nickel oxide. From the results obtained from experiments with mixtures of titania with nickel in the present study it was found that very active catalysts were obtained by the addition of from 20 per cent to 50 per cent titania.

Much work has been reported in the literature upon the adsorption of carbon monoxide by copper and copper oxide, and the catalytic activity of copper oxide toward the oxidation of carbon monoxide. Bone and Andrew in their experiments with copper and copper oxide in the catalytic combustion of carbon monoxide found that copper oxide was an active catalyst at 170°C.

The results from experiments of mixtures of titania with copper oxide at 300°C. and 150°C. may be seen in Tables III and IV. The addition of 1 per cent of copper oxide to titania produced a very active catalyst. Mixtures of titania with copper oxide were found to be very good catalysts at temperatures slightly above room temperature. The data in Table V are the results from experiments carried out at a temperature of 50-60°C. It may be observed that the mixture of 60 per cent titania with 40 per cent copper oxide exhibited the greatest activity.

TABLE V

Experiments with Titania and Copper Oxide at 50-60°C.

CO-air mixture, dry. CO, 10-12 per cent. One gram of catalyst used. Duration of run, two hours. Temperature of ignition, 300°C.

Catalyst	Percentage of Oxidation
TiO_2 90% + CuO 10%	0.0
TiO_2 80% + CuO 20%	87.0
TiO_2 70% + CuO 30%	14.9
TiO_2 60% + CuO 40%	98.6
TiO_2 50% + CuO 50%	93.1
TiO_2 40% + CuO 60%	92.7
TiO_2 20% + CuO 80%	79.6

Effect of Water Vapor upon Titania-Copper Oxide Catalysts. It has been pointed out by previous workers on the catalytic oxidation of carbon monoxide that water vapor has the effect of cutting down the reaction velocity. This was found to be true in the present investigation when working at a temperature of 50°C. It is quite evident from an inspection of Table VI that water

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[9] R. N. Pease and H. S. Taylor: Promoter Action in Catalysis, J. Phys. Chem., **24**, 241-265 (1920).

[10] W. A. Bone and G. W. Andrew: loc cit.

vapor has a marked retarding effect upon the catalytic activity of titania-copper oxide catalysts at 50°C. This effect was removed by working at a higher temperature. The same catalyst which previously had shown little or no activity at 50°C. in the presence of water vapor oxidized completely a carbon monoxide-air mixture saturated with water vapor when the temperature was raised to 150°C. and continued with 100 per cent efficiency after ten to twelve hours' use with a gas mixture saturated with water vapor.

<div align="center">

TABLE VI

Experiments to show the Effect of Water Vapor upon Titania-Copper Oxide Catalysts
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Experiment	Catalyst	Percentage of Oxidation at 50-60°C.	
		2 hrs.	4 hrs.
	CO-Air Mixture Dry		
1	TiO$_2$ 40% + CuO 60%	80.0	82.5
2	TiO$_2$ 60% + CuO 40%	85.1	100.0
3	TiO$_2$ 60% + CuO 40%	92.7	100.0
	CO-air Mixture saturated with Water Vapor		
4	TiO$_2$ 40% + CuO 60%	76.7	0.0
5	TiO$_2$ 60% + CuO 40%	69.0	0.0
6	TiO$_2$ 40% + CuO 60%	72.0	0.0
7	TiO$_2$ 60% + CuO 40%	73.4	10.9

Discussion of Results

In all, between 250 and 275 experiments were carried out in the apparatus described, following a uniform procedure. The results of the experiments with the separate oxides, nickel oxide, cobalt oxide, cupric oxide, and hopcalite were in good agreement with those obtained by previous investigators. The results of the study of the retarding effect of water vapor show certainly that the inhibiting effect of water vapor may be attributed to the adsorption of the water vapor upon the catalytic surface. The results with titania mixed with the various metallic oxides emphasize the superiority of mixed oxides in the catalytic oxidation of carbon monoxide and serve again to illustrate the "mixture effect." It would be difficult and hazardous to explain just what part titania has in a mixture such as has been described for titania-copper oxide. It is probable that the surface of the copper oxide has been greatly activated. The net result of such a mixture has been a catalyst with high activity toward the catalytic oxidation of carbon monoxide.

Summary

A qualitative study has been made of the catalytic activity for the oxidation of carbon monoxide by titania and mixtures of titania with a number of

metallic oxides.[11] The important points brought out in this investigation are summed up as follows:

1. Titania has been shown to be a moderately good catalyst for the oxidation of carbon monoxide at a temperature of about 300°C. The inhibiting effect of small amounts of H_2S and other laboratory fumes on the preparation of the catalyst has been pointed out.

2. Preliminary experiments with titania in mixtures with chromium oxide, cerium oxide, and uranium oxide indicated little advantage over that of titania alone.

3. Mixtures of titania with ferric oxide function as catalysts for the oxidation of carbon monoxide at temperatures much below that at which these oxides are singly catalytically active.

4. Nickel oxide has been shown to exhibit greater catalytic activity by the addition of titania.

5. The results of experiments of mixtures of titania with copper oxide in this investigation show that very active catalysts for the oxidation of carbon monoxide can be obtained. They show undiminished activity at a temperature of 150°C. in the presence of water vapor after twelve hours of continuous use.

6. The inhibiting effect of water vapor upon the titania-copper oxide catalysts has been studied. At temperatures of about 50°C. there is a very marked retarding effect.

7. A comparison of the results obtained from catalysts prepared by different precipitants has been made.

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[11] Letters patent have been applied for in the U. S. Patent Office to cover the preparation and use of this catalyst.

CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE—II

BY C. J. ENGELDER AND MANUEL BLUMER[*][†]

Continuation of the work upon the catalytic oxidation of carbon monoxide begun in this laboratory by Miller led to further results which are here reported.   Further examination of Miller's titania-copper oxide catalyst showed it to be unsatisfactory for use at high temperatures and the search for a better catalyst resulted in the one described below.

Lamb, Bray, and Frazer,[1] and their associates in their development of the catalyst called Hopcalite, which consists of a mixture of manganese dioxide and cupric oxide, conducted most of the investigations which culminated in the production of this well known catalyst.   The same investigators performed much of the later work which dealt with the various factors influencing the catalytic activity of Hopcalite.

Bone and his co-workers[2] studied the combustion of carbon monoxide with oxygen using nickel, copper, and their oxides as catalysts.   Other interesting contributions on this subject have been made by Benton[3] who studied the adsorption of carbon monoxide by oxide catalysts.   The effect of water vapor upon the catalytic activity of oxide catalysts was investigated by Merrill and Scalione.[4]   Lamb and Vail[5] also studied the effect of moisture upon Hopcalite.

Oxides of manganese, cobalt, and nickel, were found to be active at low temperatures when purified by an electro-endosmosis method developed by Bennet.[6]   A two-component catalyst containing ferric and chromium oxides was shown by Frazer[7] to be active at elevated temperatures.

1 A. B. Lamb, W. C. Bray and J. C. W. Frazer: "The Removal of Carbon Monoxide from the Air," J. Ind. Eng. Chem., 12, 213-221 (1920).

2 W. A. Bone and G. W. Andrew: "Studies in Catalytic Combustion, II.   The Union of Carbon Monoxide and Oxygen in Contact with Nickel, Copper, and their Oxides," Proc. Roy. Soc., 110-A, 16-34 (1926).

3 A. F. Benton: "Adsorption of Gases by Oxide Catalysts," J. Am. Chem. Soc., 45, 887-900 (1923).

4 D. R. Merrill and C. C. Scalione: "The Catalytic Oxidation of Carbon Monoxide at Ordinary Temperatures," J. Am. Chem. Soc., 43, 1982-2002 (1921).

5 A. B. Lamb and W. E. Vail: "The Effect of Water and Carbon Dioxide on the Catalytic Oxidation of Carbon Monoxide and of Hydrogen by Oxygen," J. Am. Chem. Soc., 47, 123-142 (1925).

6 O. G. Bennet: "Catalysts for Low Temperature Oxidation of Carbon Monoxide," Thesis, Johns Hopkins University (1930).

7 J. C. W. Frazer: "Method of eliminating Combustible Constituents from the Products of Combustion of an Internal Combustion Engine," U. S. P. 1,789,812, Jan. 20, 1931.

Preparation of Catalyst. Single oxide catalysts were prepared by precipitation as hydroxides from aqueous solutions, ammonium hydroxide being used wherever possible. The precipitates were washed free from electrolytes, filtered by suction and dried at 100°C. After crushing to 12-20 mesh they were activated at 300°C. for 1 hour in an air stream containing 10 per cent carbon monoxide. Two-component catalysts were in general precipitated simultaneously by the use of appropriate reagents and treated in the manner just described.

Method of testing Catalyst. The oxide catalysts included in Table I were tested by passing a carbon monoxide-air stream, containing 10 per cent carbon monoxide by volume, at 2 liters per hour over 1 gram of catalyst contained in a glass tube inserted into an electrically heated furnace. The gas stream was dried by passing it through concentrated sulfuric acid, calcium chloride, and phosphorous pentoxide. The effluent gas was analyzed for carbon dioxide and carbon monoxide.

TABLE I

Per Cent Oxidation of Carbon Monoxide by Oxide Catalysts

Catalyst	Per Cent Oxidation at Temperatures					
	400	300	200	100	50	0°C.
Single-Oxide Catalysts						
WO$_3$	—	0	0	0	—	—
BeO	—	3.4	0	0	—	—
HgO	—	Dec.	0	—	—	—
ZrO$_2$	—	51.0	0	0	0	—
CuO	—	56.0	33.0	—	—	—
V$_2$O$_5$	—	60.0	0	0	0	—
Ag$_2$O	—	76.0	0	—	—	—
NiO	—	89.0	98.0	91.0	20.0	—
ZnO	—	100.	25.0	0	—	—
TiO$_2$	—	95.0	—	—	—	—
MnO$_2$	—	100.	100.	85.0	71.0	—
Cr$_2$O$_3$	—	100.	34.0	0	—	—
Fe$_2$O$_3$	—	100.	100.	26.8	0	—
Co$_2$O$_3$	—	89.0	76.0	78.0	78.0	—
Two-Component-Oxide Catalysts						
Fe$_2$O$_3$ − MnO$_2$	67.0	100	100	100	100	50.0
Fe$_2$O$_3$ − NiO	—	100	82.5	4.0	0	—
Fe$_2$O$_3$ − Co$_2$O$_3$	100	100	95.0	100	100	85
Fe$_2$O$_3$ − V$_2$O$_5$	—	100	15.0	0	0	—
Co$_2$O$_3$ − MnO$_2$	100	95.0	100	100	100	0
Co$_2$O$_3$ − NiO	100	100	100	100	81.5	0
Co$_2$O$_3$ − V$_2$O$_5$	—	100	100	80.5	45.0	—
MnO$_2$ − NiO	100	95.0	100	100	100	—
NiO − V$_2$O$_5$	—	100	100	62.0	0	—

The activity of the catalysts, tested at various temperatures, using a gas mixture containing 10 per cent carbon monoxide by volume, at 2 liters per hour, is given in Table I. All the two-component catalysts listed in this table contained equal parts by weight of the two constituents.

Of the single oxides tested, many exhibited a high degree of activity at the higher temperatures, the activity generally decreasing very rapidly as the temperature was lowered. The five most promising oxides were used in the preparation of the two-component catalysts.

The two-component catalysts proved to be highly active over a large temperature range. The catalyst containing cobaltic and ferric oxides being chosen as the most promising of the series, further efforts were concentrated upon this catalyst.*

The proportions of cobaltic oxide and ferric oxide were varied in a series of catalysts, the results being given in Table II. The catalyst containing 30 per cent Co_2O_3 and 70 per cent Fe_2O_3 was the most active at low temperatures, oxidizing 95 per cent of the carbon monoxide at 0°C.

TABLE II

Activity of Catalysts containing Varying Proportions of Cobaltic Oxide and Ferric Oxide

No.	Per Cent Co_2O_3	Per Cent Fe_2O_3	Per Cent Oxidation at Temperatures					
			400	300	200	100	50	0°C.
1	10	90	100	100	89.0	16.2	0	—
2	30	70	100	100	94.0	94.0	94.0	95.0
3	50	50	100	100	95.0	100	100	85.0
4	70	30	100	100	100	100	100	89.0
5	90	10	100	100	100	100	100	74.0

Air containing 10 per cent carbon monoxide by volume, and saturated with water vapor at room temperature, was passed over the freshly activated catalyst (30 : 70 Co_2O_3 − Fe_2O_3) for a period of 10 hours, no drying agent being used, with no decrease in the activity of the catalyst. The heat of reaction when carbon monoxide is oxidized to carbon dioxide maintains the catalyst at a temperature sufficiently high to prevent water adsorption.

Activity of Catalyst using Modified Bureau of Mines Test. 1. At 0°C. using ½ per cent carbon monoxide by volume.—The catalyst containing 30 per cent cobaltic oxide and 70 per cent ferric oxide was used in all the following experiments. A glass tube 3 cm. in diameter and 25 cm. long, to the bottom of which a glass spiral, made of 125 cm. of 5 mm. tubing was attached, was used as the catalyst container. The drying agent and catalyst being placed inside the large tube, the entire apparatus was placed in crushed ice to maintain a temperature of 0°C. Air saturated with water vapor containing ½ per cent by volume of carbon monoxide, was passed at 250 liters per hour through the

* Letters patent have been applied for in the U. S. Patent Office to cover the preparation and use of this catalyst.

spiral to cool it to 0°C., then through the catalyst tube. A carbon monoxide indicator, described by Katz[8] and his co-workers was used to indicate carbon monoxide in the effluent gas.

As Table III shows, the catalyst completely oxidized the carbon monoxide as long as the drying agent delivered dry gas. Doubling the quantity of drying agent doubled the time during which the catalyst was active. Upon reactivation, the catalyst regained its former activity.

TABLE III

Activity of Catalyst at 0°C.

Rate of flow—250 liters per hour
Concentration of CO—½ per cent by volume

Test No.	Wt. of Catalyst (grams)	Per Cent Conversion at End of			
		1 hour	2 hours	3 hours	4 hours
1	17.0	99.5	99.0	99.0	95.0
2	17.0	100.	100.	98.3	97.0
3	15.0	99.5	95.0	—	—
4	13.0	98.0	95.0	—	—
5	8.5	97.0	—	—	—

2. At room temperature using 1 per cent CO by volume.—A series of tests using gas of 50 per cent relative humidity at room temperature and containing 1 per cent carbon monoxide by volume were made using the same general procedure as in the 0°C. tests. These tests emphasize the sensitivity of the catalyst used to small amounts of water vapor, the life of the catalyst depending upon the quantity and quality of drying agents used.

The results obtained by these tests are included in Table IV.

TABLE IV

Activity of Catalyst at Room Temperature

Rate of flow—250 liters per hour
Concentration of CO—1 per cent by volume

Test No.	Wt. of Catalyst (grams)	Per cent conversion at end of		
		0.5 hour	1.0 hour	1.5 hours
1	17.0	100	97.0	88.5
2	17.0	97.5	88.5	85.0
3	17.0	99.0	98.0	95.0
4	17.0	98.0	97.0	93.0
5	17.0	99.0	98.0	95.0
6	17.0	97.0	95.0	—
7	17.0	98.0	95.0	—

[8] S. H. Katz, D. A. Reynolds, H. W. Frevert and J. J. Bloomfield: "A Carbon Monoxide Recorder and Alarm," Dept. Commerce, Paper 355 (1926).

It was found that a catalyst which had decreased in activity to 95 per cent had adsorbed 0.17 g. of water, which was 1 per cent of its weight, and became completely inactive when 2.5 per cent of its weight of water had been adsorbed. This explains the longer life at 0°C., as air of 50 per cent relative humidity at 20°C. contains approximately 4 times more water vapor than saturated air at 0°C. As the same quantity of drying agent was used, the catalyst life at room temperature should be approximately one-fourth that of 0°C. Using a large excess of drying agent, the catalyst maintained its initial activity for a period of 8 hours, at which time the drying agent was exhausted.

3. *Catalyst Activity using High CO Concentrations.*—As previously mentioned, with relatively high concentrations of carbon monoxide, the heat liberated by the oxidation of the carbon monoxide on the catalyst granules is sufficiently high to prevent water adsorption. It was found that when air at 20°C., of 50 per cent relative humidity, containing 3 per cent of carbon monoxide, was passed over the catalyst, its temperature was raised to approximately 250°C., and suffered no loss in activity at the end of eleven hours, although no drying agent was used.

Higher carbon monoxide concentrations were used, up to 20 per cent, the catalyst temperature increasing to 890°C. with the latter concentration, with no decrease in activity. At elevated temperatures it was possible to increase the gas flow to 50 liters per gram of catalyst and still obtain complete oxidation of the carbon monoxide.

4. *Supported Catalysts.*—Supported catalysts were prepared by adding the inert material, usually in the form of 12 to 14 mesh granules, to an aqueous solution of the nitrates of cobalt and iron in the proper proportion, and evaporating the solution to dryness. The impregnated granules were activated by maintaining the granules at 175°C. for 10 hours. Asbestos fiber, steel chips, pumice granules, and crushed fire brick were used as catalyst supports.

Tests at high temperatures (500-600°C.), using the catalytic pumice granules, showed that one gram of oxide catalyst coated upon 50 cc. of pumice granules was capable of completely oxidizing the carbon monoxide in a 3 per cent gas stream flowing at 250 liters per hour.

Catalyst coated upon asbestos fiber was equally active, but had a much higher resistance to gas flow.

Fire brick granules had a tendency to react with the oxide catalyst, at high temperatures, reducing its activity within a few hours.

Metallic supports, such as iron chips or screens, oxidized at the temperature used in the tests; the iron oxides formed peeled off, thus removing the catalytic surface.

Summary

1. A study has been made of a large number of oxides which function as catalysts for the oxidation of carbon monoxide.

2. The activity of single oxide catalysts, especially manganese dioxide, ferric oxide, cobaltic oxide, and nickelous oxide, were in good agreement with results obtained by previous investigators.

3. A catalyst containing 30 per cent cobaltic oxide and 70 per cent ferric oxide was found to have a high degree of activity at temperatures ranging from 0°C. to 200°C., using a thoroughly dried gaseous mixture containing ½ to 2 per cent carbon monoxide. In the above temperature range it was rapidly poisoned by water vapor, one per cent of the catalyst weight of water being sufficient to decrease its activity to 95 per cent, 2.5 per cent of water rendering it completely inactive.

. 4. The adsorption of water vapor, which caused a decrease in catalytic activity, was reversible, reactivation at 300°C. for 1 to 2 hours restored its previous activity.

5. When the concentration of carbon monoxide was 3 per cent or higher, no drying agent was required, as the heat of reaction was sufficient to prevent water adsorption from a gaseous mixture of 50 per cent relative humidity at room temperature.

6. At elevated temperatures, ranging from 200° to 850°C., complete oxidation was obtained using rates of gas flow as high as 50 liters per hour per gram of catalyst, the gas containing up to 20 per cent carbon monoxide.

7. Catalytic material coated upon asbestos fiber and pumice granules exhibited high activity at elevated temperatures.

CRITICAL CONSTANTS AND VAPOR PRESSURE
OF BORON TRIFLUORIDE

BY HAROLD SIMMONS BOOTH AND JAMES M. CARTER

In view of the fact that a careful search of the literature failed to reveal any determination of the critical constants and vapor pressure of boron trifluoride, it seemed advisable to determine these constants.

Preparation of Boron Trifluoride

Boron trifluoride was prepared essentially as done by Germann and Booth.[1] Crystal boric acid from Asia Minor ore (kindly supplied by the Pacific Coast Borax Company) was dehydrated by fusion. The powdered fused boric oxide was then dissolved in hot concentrated sulphuric acid. When cold this was mixed with powdered fluorspar in a large porcelain mortar. The heat of reaction was sufficient to cause the evolution of most of the silicon fluoride. When this ceased and before the mass set, it was poured into a generating flask connected to the apparatus by a universal conical joint. The flask was then heated with a free soot flame and the gas passed through a reflux condenser (to separate volatile liquids), through a wash bottle containing boric oxide dissolved in sulphuric acid to remove hydrogen fluoride, and condensed by means of liquid air in the gas-fractionating tube.[2] The boron fluoride was then fractionally distilled rejecting the first and last portions until clear and free from apparent impurities. Usually six distillations were sufficient for this purpose but several more were made.

Preparation of Samples

Sample I was boron trifluoride thus purified and stored for six months before use. This gas was transferred to a separate fractionating apparatus, condensed with liquid air, and fractionated eight times more with generous discarding of the first and last fractions. Both the apparatuses for handling boron trifluoride were previously dried by rinsing twelve times with air which had passed slowly through tubes filled with broken stick potassium hydroxide, calcium chloride and then barium oxide.[3] Experience has shown this is ample rinsing.

The Cailletet tube, which had previously been sealed on to the apparatus with an intervening stopcock close to the tube and carefully dried at the same time as the apparatus, was rinsed with small amounts of the middle fractions of boron trifluoride at each distillation with thorough evacuation before the next rinsing, to insure removal of adsorbed air. The middle part of the middle fraction of the ninth distillation was used for a final rinse and then the

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[1] Germann and Booth: J. Phys. Chem., **30**, 369 (1926).

[2] For details of such an apparatus see J. Phys. Chem., **30**, 369 (1926) and J. Chem. Ed., **7**, 1259 (1930).

[3] "Barium Oxide as a Desiccant," H. S. Booth and L. H. McIntyre: Ind. Eng. Chem., Anal. Ed., **2**, 12 (1930).

Cailletet tube was filled from this middle part of the middle fraction to within one or two centimeters of atmospheric pressure. The stopcock of the Cailletet tube was then closed and the space intervening between it and the fractionating apparatus carefully rinsed twelve times with carbon dioxide-free dry air before breaking off the Cailletet tube.

Sample II was prepared in the same way save in two respects: First, the mixture in the generator was heated by a water bath while evacuating the system to insure elimination of silicon tetrafluoride before heating with a soot flame to the temperature of boron trifluoride generation; and second, only one day elapsed between the generation and the first fractionation, and the final fractionation and filling of the Cailletet tube. Immediately after filling, the Cailletet tube was removed from the apparatus, and the stopcock broken off under mercury, to avoid any contamination by grease.

Keeping the open end of the tube under mercury, it was placed in the steel container attached to the pump and manometer.[1] It was found that the gas had no corrosive effect on mercury, even at high pressures, and over considerable periods of time. It was also found, as is usual with absolutely dry fluorides, that the glass was not attacked. What was more surprising, however, was that the stirrer used to accelerate equilibrium,[2] consisting of a small chromium-plated iron rod, was not attacked.

Measurement of Pressure and Temperature

The manometer used was one of the absolute type, manufactured by Schaffer and Budenburg. The size of the piston had been measured with micrometer calipers at various points, and the weights compared with a standard kilogram. In addition it had been compared with a closed Amagat type manometer, and found to agree to within the limits of experimental error, (slightly less than 0.1 atm.). The range of the Schaffer and Budenburg manometer used was such that it did not operate satisfactorily at pressures below ten atmospheres.

Temperatures were measured by means of a P.T.R. Anschütz thermometer, which was subsequently checked against a resistance thermometer calibrated by the Bureau of Standards. The P.T.R. thermometer could be read to .02°C. One point, at $-50°$, was measured on a liquid in glass thermometer, and is slightly more doubtful than the others. It was thought that the thermometer contained alcohol, but the readings below $-45°$ were erratic unless the thermometer had been cooled from room temperature to the temperature of test immediately before reading. The one reading retained fulfilled this condition; others taken after the thermometer had been cold for some time, were discarded.

Experimental Procedure

After placing the thermostat around the experimental tube, the temperature was held constant, and the gas compressed. When a temperature had

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[1] The Cailletet apparatus was the same as that used by the authors in determining the Critical Constants of Carbon Dioxide-Oxygen Mixtures, J. Phys. Chem., **34**, 2801, 2813 (1930).

[2] Kuenen: Arch. néerl., **26**, 394 (1892); Z. physik. Chem., **11**, 38 (1893).

been reached at which the gas could be liquefied, the pressure was adjusted until the liquid and gas phases were equal in volume. The temperature was then raised very slowly, and the temperature at which the liquid disappeared was noted. The mixture was stirred vigorously, as equilibrium is only obtained very slowly otherwise. After the critical point had been passed, the pressure was maintained at the same value, and the temperature was gradually lowered, until the meniscus reappeared in the tube.

The critical pressure could be determined extremely accurately by this method. If the pressure chosen was too low, the meniscus moved down the bulb as the temperature was increased, and disappeared at the bottom, while if the pressure was too high it moved upward and disappeared at the top. The limits between which it remained near the middle of the tube were quite narrow, and varied by not more than 0.05 atm.

In determining the vapor pressures at lower temperatures, the pressure taken was that which made the volume of gas and liquid equal. Here again, the pressure limits from all gas to all liquid were extremely narrow. The slightest addition of weight to the manometer was sufficient to send the meniscus from the bottom to the top of the bulb.

The critical opalescence was clearly observed. Especially on cooling, the opalescence was marked, as the gas appeared to be supersaturated. If it was not stirred it remained heavy and foggy, and no noticeable liquid separated until the critical temperature had been passed. On stirring, however, the liquid phase separated immediately.

It was noticed that near the lowest temperatures reached ($-50°C.$), the liquid appeared quite viscous. The stirrer tended to stick to the walls of the bulb unless it was kept in motion continuously. This probably indicates association of the liquid boron trifluoride at this pressure and temperature. At the boiling point, boron trifluoride is not viscous and is probably little associated.

Results

The results of the determinations of the critical constants and the vapor pressures are given below. Two gas samples were used, which had been purified separately, and several runs were made on each. In the case of Sample II the critical point and vapor pressure curve were redetermined after the gas had stood in the Cailletet apparatus in contact with glass and mercury for a week (Oberservations IIb). No change was found. The observations (cor.) of the critical temperatures and pressures are shown in Table I. The data for the vapor pressures are given in Table II.

The average of the determinations of the critical temperature was found to be $t_c = -12.25°C.$ Variation $\pm 0.03°$. Critical pressure $p_c = 49.2$ atm. (I.C.T. normal) Variation ± 0.1 atm.

The equation for the vapor pressure curve was found to conform to $\log_{10} P = 5.1009 - 0.8896 \cdot 1000/T$. According to the International Critical Tables, Volume 3, p. 232, boron trifluoride has a vapor pressure of 1 atmosphere at $-101°C$. The vapor pressure at $-101°C$. was calculated by this equation to be 0.8484 atmospheres. Obviously this comparison of the ob-

served and calculated vapor pressures at the boiling point shows that the equation is satisfactory for low pressure data as well as those it was made to fit.

Calculation of Heat of Vaporization

The vapor pressure equation:

$$\log_{10}P_{atm} = 5.1009 - \frac{0.8896}{T} \cdot 1000,$$

may be differentiated to give

$$\frac{d(\log_{10}P)}{dT} = + \frac{889.6}{T^3}$$

TABLE I
Critical Constants of Boron Trifluoride

	Temperature determinations	Pressure determinations
Sample	t_c	P
I	$-$ 12.25°C.	49.0 atm. (I.C.T.
I	$-$ 12.25	49.2 normal)
I	$-$ 12.20	
II	$-$ 12.25	49.1
II	$-$ 12.20	49.3
I	$-$ 12.30	
IIb	$-$ 12.30	49.2
Av.	$-$ 12.25°C. $\pm$ .03°	49.16 $=$ 49.2 atm.
		$\pm$ .1 atm.

TABLE II
Vapor Pressure of Boron Trifluoride

$t°$	P atm.	Sample
$-$ 12.25	49.0	I
20.12	38.5	I
39.20	20.5	II
12.25	49.2	I, II
12.20	49.1	I, II
49.25	13.8	II
38.50	22.5	II
30.11	28.5	II
20.22	38.7	II
39.25	19.8	IIb
35.08	23.2	IIb
35.00	23.8	IIb
35.19	23.8	IIb
29.96	27.9	IIb
29.76	28.2	IIb
19.92	38.6	IIb
19.95	38.6	IIb
14.65	45.4	IIb
14.60	45.5	IIb

which may be compared with the approximate Clapeyron equation:

$$\frac{d(\log_e P)}{dT} = \frac{H_{vap}}{RT^2}$$

It is seen that $H_{vap} = 889.6R \cdot \log_e 10$
or $\qquad H_{vap} = 4057$ cal./mol.
$\qquad\qquad = 59.93$ cal./gm.

This value may be expected to be reasonably correct at a temperature where the assumptions of negligible liquid volume, and perfect gas behavior for the vapor may be reasonably close to the facts. This will probably be the case near the normal boiling point.

Summary

1. As a result of seven determinations it has been found that the critical temperature of boron trifluoride is $-12.25°C. \pm 0.03°$, and the critical pressure 49.2 atmospheres (I.C.T. normal) ± 0.1 atmosphere.

2. The vapor pressures have been determined from the critical pressure down to 10 atmospheres. The equation for the vapor pressure was found to be $\log_{10} P = 5.1009 - 0.8896 \cdot 1000/T$.

3. Dry boron trifluoride was found to have no corrosive effect on mercury, chromium plating, or glass even at high pressure and over considerable periods of time.

4. The heat of vaporization of boron trifluoride was calculated to be 4057 cal./mol.

5. It was noticed that near the lowest temperature reached, $-49.25°C.$, at a vapor pressure of 13.8 atmospheres the boron trifluoride became noticeably viscous, probably indicating some association.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.

A STUDY OF THE MAGNITUDE OF THE CROWDING EFFECT IN CURRENT FLOW THROUGH SMALL TUBES AND SLITS*

BY H. L. WHITE, L. C. VAN ATTA AND E. A. VAN ATTA

In 1929 McBain, Peaker and King[1] reported that for 0.001 N aqueous solution of KCl at 25° the extra conductance in the neighborhood of optically polished glass corresponded to a specific surface conductance of 4.3×10^{-8} mhos. This value was determined by measuring the resistance of a cell filled with solution and containing a removable narrow glass slit of known dimensions. According to these authors three factors operate to make the observed resistance of cell plus slit filled with dilute salt solution different from the calculated resistance of the slit alone, the calculation being based on the specific resistance of the solution and the measured dimensions of the slit. The first of these factors is obviously the resistance of the cell alone. The second factor is the enhanced conductance at or near the glass-water interface, i.e. the surface conductance, appreciable only at low concentrations. The third factor is the "pinch" effect, "operating in all concentrations, and due to bending of the lines of current flow through the slit, and equivalent to a series resistance." The second factor operates to make the observed resistance less than the calculated, the third to make it greater. The present paper is an experimental and theoretical consideration of the third factor or pinch effect.

In order to confine ourselves to the pinch effect we shall consider in this paper only those experiments of McBain, Peaker and King in which concentrated (1.0 N or 0.1 N KCl) solutions were used. At these concentrations these authors assumed the surface conductance would be a negligible fraction of the normal or volume conductance and we shall prove in this paper that this assumption is correct. To consider a representative case, they find that with 1.0 N KCl the resistance of cell plus slit no. 5 is 204.45 ohms. The calculated resistance of the slit is 162.79 ohms, which leaves a cell resistance of 41.66 ohms. But when the resistance of the cell alone is determined it is found to be only 14.14 ohms. This means that the effective resistance of the cell has been increased by 27.52 ohms due to the presence of the slit, apart from the actual resistance of the slit. This increase is called the pinch effect. The sum of pinch effect and of resistance of cell alone is termed the "effective resistance." The effective resistance of a given cell plus slit should be proportional only to the specific resistance of the solution used. If then it is determined with a concentrated solution it can be calculated for a dilute solution. This calculated figure is subtracted from the observed resistance of cell plus slit for dilute solution to give the resistance of the slit alone. The figure so obtained is compared with the calculated resistance of the slit for the dilute solution and

found always to be lower. The increase in specific conductance in the slit may be as much as 53 per cent above normal for a 0.0125 mm. slit and 0.001 N KCl and is ascribed to surface conductance.

The results of McBain, Peaker and King with regard to pinch effect will be considered more in detail after a theoretical consideration of the expected magnitude of the effect. Because of certain inconsistencies in the results, to be discussed later, it is desirable to use, for a study of the influence of surface conductance on the measured resistance, an apparatus in which pinch effect is negligible.

In place of slits we have used pyrex capillaries ranging from 0.008 to 0.096 mm. bore. These offer several advantages over the slits. First, the technical difficulties which McBain, Peaker and King experienced in preparing and preserving their material are avoided. We had considerable trouble while we were drawing our own capillaries but our difficulties of preparation were practically eliminated by the cooperation of the Corning Glass Works in supplying us with tubing of outside diameter from 6 to 7 mm. and inside ranging in small steps from 0.005 to 0.100 mm. A second advantage is that the resistance of the cell or holder plus connections is a negligible fraction of the whole, less than 1 part in 10,000; this eliminates one of the factors. Third, there is no danger that cracks will develop. Fourth, higher values of the surface to volume ratio are attainable. And fifth, it will be shown that pinch effect is entirely negligible. The electrical connections to the capillary, its preliminary treatment, the procedure of filling it with solution, method of resistance determinations, etc., are described in the following paper.

In the present work direct current has been used. This avoids a number of complications, but raises the question as to whether the results have been affected by polarization. There is ample evidence that polarization is not a disturbing factor. In the first place the sum of the resistances of two parts of a broken capillary equals that of the whole. Further proof has been obtained directly from the electrometer which shows no deflection when a capillary is thrown into its circuit immediately after the capillary has had a constant EMF impressed upon it for several minutes. This is true for resistances as high as 10^{11} ohms.

The dimensions of seven capillaries of from 0.0080 to 0.0964 mm. bore were measured. Lengths of the order of 25 mm. were measured to 0.1 mm. with a micrometer caliper, diameters were measured at each end with a screw micrometer eye-piece and either a 16 or a 3 mm. objective. Several measurements at each cross section were made by two independent observers. The mean value of these measurements is probably less than 1 per cent from the true value for the larger capillaries and not more than 2 per cent for the small. The cross section is usually not completely circular but the eccentricity is small; in all these capillaries the area of the elliptical cross section differs by considerably less than 1 per cent from the calculated circular area, using the arithmetic mean of the major and minor axes as the diameter. The cross sectional areas of each end are of almost the same value; their average has been taken as mean cross sectional area. Thus it is possible to measure the resis-

tance of a column of solution of known concentration, and also to calculate this resistance from a knowledge of capillary dimensions and specific resistance. Such measurements have been carried out and in every case the observed resistance agreed with the calculated, as is seen in Table I. The specific resistance at 25° of 1.0 N KCl is taken as 8.95, of 0.1 N KCl as 77.8 ohms; the observed resistances have been reduced to 25°. The measurements on 57a, 57b, 58, 58a and 58b with 1.0 N KCl were with a Wheatstone bridge, the others by the condenser rate of charge method. Each figure represents the average of a number of closely agreeing determinations.

TABLE I

Cap No.	Mean diameter by microscopic measurement mm.	length cm.	Calculated resistance with 1.0 N KCl ohms	Observed resistance with 1.0 N KCl ohms	Calculated resistance with 0.1 N KCl ohms	Observed resistance with 0.1 N KCl ohms
56	0.0078	1.40	2.63×10^7	2.50×10^7		
57	0.0398	4.45	3.21×10^6	3.27×10^6		
57a	0.0396	1.97	1.43×10^6	1.44×10^6	1.245×10^7	1.26×10^7
57b	0.0398	2.48	1.79×10^6	1.805×10^6	1.56×10^7	1.59×10^7
58	0.0964	4.77	5.85×10^5	5.87×10^5		
58a	0.0964	1.90	2.33×10^5	2.36×10^5	2.02×10^6	2.05×10^6
58b	0.0964	2.84	3.49×10^5	3.40×10^5	3.04×10^6	3.08×10^6

These results mean either that both surface conductance and pinch effect are absent or that they just cancel each other. That the latter is not the case is evident from the following consideration. Surface conductance becomes less prominent as capillary diameter increases, while pinch effect becomes more prominent; this latter statement will be proved in the theoretical discussion. Therefore these two factors, if present to an appreciable extent, could cancel each other only at a certain capillary diameter; the observed resistance of capillaries of diameters greater than this should be greater than the calculated and vice versa. Since no resultant effect appears at any diameter it follows that neither is present.

Another proof of absence of pinch effect follows. If pinch effect is present it will be manifested at each end of a capillary; the sum of the effects at each end may be called the pinch effect for that capillary. If now the capillary is broken into two pieces the sum of the two resistances should exceed the original resistance by one pinch effect, whether or not surface conductance exists and independent of any accurate measurements of capillary diameter. If it is shown that the sum of the two resistances equals the original, pinch effect is negligible. This is shown in Table I. Capillaries 57a and 57b are the two fragments into which 57 was broken; 58a and 58b are from 58. It will be seen that the sum of the observed resistances with 1.0 N KCl of 57a and 57b practically equals the resistance of 57; the same is true for the fragments of 58.

In view of McBain, Peaker and King's findings it is surprising that in our work repeated determinations consistently show the observed resistance to agree with the calculated. It is possible to predict a pinch effect from theoretical considerations, and to calculate the magnitude of such an effect for the capillaries used in the present experiment. This problem has been treated theoretically by Lord Rayleigh.[2,3]

In general, the measured resistance of a tube or slit terminating in a semi-infinite conductor of the same material may be written

$$R = R_1 + 2R_2 \tag{1}$$

where R_1 = the resistance within the tube
R_2 = additional resistance at either end due to crowding of lines of flow (pinch effect).

The resistance within the tube is given by

$$R_1 = \rho \, l/A \tag{2}$$

where ρ = specific resistance of the medium
l = length of tube
A = cross sectional area of tube.

The additional resistance at either end may be expressed in terms of C, the electrostatic capacity of an isolated disc identical in shape and area with the cross-section of the tube

$$R_2 = \rho/2\pi C \tag{3}$$

Hence the fractional error introduced by pinch effect into the measurement of R_1 is, by (2) and (3)

$$E = 2R_2/R_1 = A/\pi l C \tag{4}$$

For the particular case of a circular tube $C = (2/\pi)\sqrt{A/\pi}$ so that

$$E_{(circle)} = \sqrt{\pi A}/2l = \pi d/4l \tag{5}$$

where d = diameter of the circular tube. Using (5), it is possible to calculate the magnitude of the error for certain numerical cases.

Capillary No. 56: d = .0078 mm. = .00078 cm., l = 1.40 cm.

$E = \pi \times .00078/4 \times 1.40 = .00044 = .044\%$ error

Capillary No. 58: d = .0964 mm. = .00964 cm., l = 4.77 cm.

$E = \pi \times .00964/4 \times 4.77 = .0016 = .16\%$ error.

The conclusion from the above calculations is that there is no theoretical ground for expecting a measurable pinch effect in the capillaries used in the present experiment, since the experimental errors range from 0.5 to 2 per cent. This substantiates the experimental findings.

McBain, Peaker and King used slits differing considerably from the circular tubes treated above, so that a further development is necessary to find

the theoretically predicted order of magnitude of the error due to pinch effect in their work. This is given by the general equation (4) above

$$E = A/\pi lC$$

where, in this case, C is the electrostatic capacity of a disc having the shape and dimensions of a cross-section of the slit.

The exact calculation of C for a rectangular disc is impossible but an approximation can be made by considering the case of an ellipse with equal area and with major and minor axes in the same ratio, a/b, as the sides of the rectangle. This proves to be a close approximation because of the fact that C is not sensitive to small changes in the shape of the disc. The ratio of the capacity of an elliptical disc to that of a circular disc *of the same area* is given by Rayleigh as

$$\frac{C_{(\text{ellipse})}}{C_{(\text{circle})}} = \frac{E_{(\text{circle})}}{E_{(\text{ellipse})}} = \frac{\pi}{2} \sqrt{\frac{a}{b}} \frac{1}{F(e)} \tag{6}$$

where $e = \sqrt{1 - (\frac{b}{a})^2}$ = eccentricity of the ellipse,

$$\text{and } F(e) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - e^2 \sin^2\phi}} .$$

Combining (5) and (6), we have

$$E_{(\text{ellipse})} = \frac{1}{l} \sqrt{\frac{b}{a} \cdot \frac{A}{\pi}} \cdot F(e) = \frac{b}{2l} \cdot F(e) \tag{7}$$

F(e), the complete elliptic function of the first kind, may be looked up in tables.[4,5] Consider the application of equation (7) to a numerical example.

Slit A: $l = 0.1$ cm. $a = 1.0$ cm. $b = .001$ cm.
  $F(e) = \ln(4a/b) = 8.3$
  $E = bF(e)/2l = .042 = 4.2\%$ error.

We are now in a position to consider the results of McBain, Peaker and King. The data for three slits with 1.0 N KCl are summarized in Table II.

TABLE II

slit no.	b width (cm.)	a length (cm.)	l thick. (cm.)	calc. slit resis. (ohms)	observed pinch effect (ohms)	observed pinch effect (per cent)	calc. pinch effect (per cent)
5	.00567	1.002	0.1033	162.79	27.52	16.9	18.0
6	.00125	1.001	0.1058	757.08	186.18	24.6	4.8
10	.00125	1.001	0.5014	3587.8	647.16	18.4	1.0

The last column gives the pinch effect as calculated from equation (7). These calculated values represent an upper limit for the pinch effect since the assumption that the slit opens into a semi-infinite fluid is not at all realized, especially when auxiliary slits are introduced. As a result of this fact the experimental values should be somewhat lower than the theoretical. Both the

observed and calculated values indicate that pinch effect cannot be neglected in the case of these slits. There agreement ends, for the calculated pinch effect is in general much lower than the observed. Furthermore, the dependence of pinch effect on the dimensions of the slit predicted by theory is not found in the observed values. For example the pinch effect in ohms should be the same for slits 6 and 10, since they are identical in cross-section. Also the pinch effect in per cent should be smaller for slit 6 than for slit 5, since in this connection a decrease in width is equivalent to an increase in thickness. The conclusion is that the observed values are not to be explained as due to pinch effect.

A search for other causes for the increased resistance is not fruitful. Since pinch resistance = observed resistance of cell plus slit − calculated resistance of slit − observed resistance of cell, it follows that an erroneously high value for the first or low values for the second and third members on the right side of the equation would give rise to an apparent pinch resistance. It is inconceivable that errors of 25 per cent could arise in determination of either cell resistance or slit dimensions. As to sources of error in observed resistance of slit plus cell, cracks in the system need not be considered, as they would make the reading too low. The capacity of the cell, since the dielectric constant of glass is less than that of water, is less when the slit is added to the cell; this decrease in capacity, since it decreases the shunt across the resistance, would increase the impedance of the system. Calculation shows, however, that this factor is too small to introduce an appreciable error; even if the cell capacity were reduced from an estimated 5×10^{-10} farads to zero the impedance where the resistance is 100 ohms would be changed less than one part in 10,000,000 and with 1,000 ohms less than 1 in 100,000. On the basis of our own failure to find a pinch effect and on theoretical considerations we believe that McBain, Peaker and King's findings on pinch effect are due to some systematic error.

Summary

Whatever the explanation for the anomalous resistance in the case of slits, the difficulty is avoided by the use of tubular capillaries. The several advantages of capillaries have been mentioned above:

1. Negligible pinch effect
2. Negligible cell resistance
3. Large attainable ratio of surface to volume
4. Absence of many technical difficulties.

Three independent proofs are advanced that there is no significant pinch effect with capillaries of from 0.008 to 0.100 mm. bore. The first proof is that the observed resistance of the capillary filled with 1.0 N or 0.1 N KCl equals the calculated, where the calculation is based upon microscopic measurements of capillary dimensions and upon the specific resistance of the solutions. The second proof is that the sum of the resistances of the two fragments into which a capillary is broken equals the original resistance. The third proof is theoretical. On the basis of the experimentally and theoretically demonstrated ab-

sence of a significant pinch effect in small capillaries, of a theoretical treatment of the case of an ellipse of great eccentricity approximating a rectangular slit, and of relations between asserted pinch effect and width of slit in McBain, Peaker and King's work which conflict with theory, we believe that their observed increases of resistance with concentrated solutions are not due to a pinch effect but to some systematic error yet undetected.

Bibliography and Footnotes

[1] J. Am. Chem. Soc., **51**, 3294 (1929).

[2] "Theory of Sound," **2** (1896).

[3] J. H. Jeans: "The Mathematical Theory of Electricity and Magnetism," 356 (1925).

[4] J. B. Dale: "Five Figure Tables of Mathematical Functions" (1904).

[5] When e is very close to unity, as in the case of a much-elongated ellipse, tables cannot be relied upon for values of $F(e)$. As shown by Andrew Gray,[6] a rapidly converging series is obtained by the transformation $k = \sqrt{1 - e^2} = b/a$. For values beyond the range of the tables high accuracy is obtained by using only the first term of the resulting series, i.e.,

$$F(e) = G(k) = \ln (4/k) = \ln (4a/b).$$

The writers are indebted to G. G. Harvey who pointed out the possibility of such a transformation.

[6] "Gyrostatics and Rotational Motion" (1918).

SURFACE CONDUCTANCE AT GLASS-SALT SOLUTION INTERFACES *

BY H. L. WHITE, FRANK URBAN AND E. A. VAN ATTA

McBain, Peaker and King[1] reported in 1929 on the increase of specific conductance of dilute KCl solutions in narrow polished glass slits. This was ascribed to surface conductance at or near the glass-solution interface, the excess of conductance becoming greater as the ratio of surface to volume increased and as the dilution became greater. The ratio of surface area in sq. cm. to volume in cc. in their narrowest slits, excluding slit S and slit 2, rejected because of breakage or cracks, was 1600 to 1; their most dilute solution was 0.001 N. The found at 25°C. a mean specific surface conductance with 0.001 N KCl of 4.3 × 10⁻⁸ mhos, with 0.002 N KCl of 5.3 × 10⁻⁸ mhos, and with 0.01 N KCl of 9.3 × 10⁻⁸ mhos, specific surface conductance being defined as that of 1 cm. square of surface. The values obtained with the various slits, from which the means were calculated, varied with 0.001 N KCl from 3.0 to 5.3 × 10⁻⁸ mhos, with 0.002 N KCl from 2.8 to 6.3 × 10⁻⁸ mhos, and with 0.01 N KCl from 1.8 to 19 × 10⁻⁸ mhos. The rapid increase in the experimental error as the solution becomes less dilute is obvious. In 1930 McBain and Peaker[2] reported that the specific surface conductance at the interface between KCl solutions and unpolished pyrex glass was 13 × 10⁻⁸ mhos with 0.001 N KCl and 20.7 × 10⁻⁸ mhos with 0.01 N KCl. The ratio of macroscopic surface area to volume with this apparatus was much lower, 93 to 1, than with the slits. The authors suggest that the higher conductances at the unpolished surfaces could be explained by the assumption that the actual surface area of ordinary pyrex tubing is 2¼ times greater than that determined by macroscopic measurements. Actually the factor would be about 3 to bring the 2 sets of data on 0.001 N KCl into agreement. We reported at the 1931 Colloid Symposium[3] on determinations of stream potentials in pyrex capillaries of various sizes which suggested that either McBain and coworkers' values for surface conductance were many times too high or that the stream potential equation $E = \dfrac{\zeta PD}{4\pi\eta\kappa}$ is invalid. The argument follows.

We made our stream potential determinations on pyrex capillaries of from 0.110 to 0.005 mm. inside diameter, using 0.0005 N KCl. We can estimate that the extrapolated value for the specific surface conductance with pyrex glass and 0.0005 N KCl according to McBain and Peaker would be not less than 1 × 10⁻⁷ mhos. Taking the specific volume resistance of 0.0005 N KCl at 25°C. as 1.35 × 10⁴ ohms, we calculate that the normal

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* The Department of Physiology and the Department of Biological Chemistry, Washington University, St. Louis.

or volume resistance of a column of 0.0005 N KCl in a 0.005 mm. capillary at 25°C. is 6.88 $\times$ 10^{10} ohms per cm. The surface resistance of such a capillary would be, taking 1 $\times$ 10^7 ohms as its specific surface resistance, 1 $\times$ 10^7/3.1416 $\times$ 5 $\times$ 10^{-4} or 6.38 $\times$ 10^9 ohms per cm. The observed resistance of a 0.005 mm. pyrex capillary filled with 0.0005 N KCl should then be, if McBain and Peaker's figures for specific surface conductance are correct, 5.82 $\times$ 10^9 ohms per cm., since the observed resistance is the resultant of the normal or volume resistance and of the surface resistance in parallel. That is, the observed resistance of this system would be 8.4 per cent of the normal or calculated resistance. This means that the conductance (resultant of volume and surface conductances) in the capillary should be 12 times the normal and since the conductance factor, κ, in the stream potential equation is in the denominator, the stream potential with a 0.005 mm. capillary should be, other factors being kept constant, only 8.4 per cent of that in a large capillary, say 0.10 mm., where surface conductance is relatively insignificant. The facts were, however, that the stream potential of a 0.005 mm. capillary was 75 to 85 per cent of that in a large capillary or about 10 times as great as would be predicted from McBain and Peaker's data. If our stream potential figures were correct they could be explained by any one of the following conditions, that McBain and coworkers' figures for surface conductance were much too high, that our glass was different from theirs, that the stream potential equation does not hold, or that some other factor or factors in the equation were changed in the small capillaries so as almost to compensate for the increased conductance if it exists. The answer depends upon the results of determinations of conductance in our capillaries under the conditions of our stream potential experiments.

In the above-cited paper we reported preliminary attempts to determine the resistance of our capillaries by determining the ratio of the potential drops across the capillary and across a known high resistance, using either a known impressed e.m.f. or the stream potential as the source of e.m.f. These measurements were not quantitatively satisfactory because our known resistances were not high enough to give a large fraction of the total potential drop. They were introduced merely to show that the "spontaneous" fluctuations in stream potential were not due to variations in conductance.

The present paper is a report of conductance measurements on pyrex capillaries of from 0.10 to 0.005 mm. bore filled with 0.0005, 0.1 or 1.0 N KCl. Since the ratio of macroscopic surface to volume in our 0.005 mm. capillaries is 8000 to 1 and our solution is twice as dilute as the most dilute used by McBain, the conditions in our experiments for bringing surface conductance into prominence should be much more favorable.

Apparatus and methods. Our first resistance measurements, as noted above, were inaccurate because of lack of suitable resistors and because of our failure to give adequate consideration to the potentials of the electrodes themselves. Considerable time was spent in attempting to make stable nonpolarizable resistances sufficiently high for our purposes. Carbon lines on paper imbedded in paraffin were satisfactory up to about 10^8 ohms but

above that they could not be used, apparently because of polarization. Greater accuracy was attained on using a series of metallic sputtered resistors $(5 \times 10^8$ to 1×10^{11} ohms) prepared by Dr. L. C. Van Atta[4] and lent us by him. These resistors give constant values and do not polarize. We eventually abandoned the potential drop ratio method because of practical difficulties which attended the method even after satisfactory standard high resistances were available.

Our next method was to measure the rate of discharge of a condenser through the unknown high resistance, which is given by the equation

$$R = \frac{t}{2.303C \log V_o/V_t}$$

where R is the resistance in ohms, t the time of discharge in seconds, C the capacity of the condenser in farads, V_o and V_s the voltages on the condenser immediately after charging and after time t, respectively. The condenser was a Leeds & Northrup standard mica, 0.1 mf. being used with the dilute solution, 1 mf. with the concentrated. The ratio V_o/V_t was taken as the ratio d_o/d_t, the ballistic deflections of galvanometer on condenser discharge; the galvanometer had a current sensitivity of 8×10^{-11} amp., a period of 12 seconds, coil resistance of 575 ohms and C.D.R. of 26,000 ohms; as used it was damped with 22,000 ohms. The calibration curve, i.e., deflection against impressed voltage, was frequently redetermined. The resistance of the condenser varied between 2.5 and 3×10^{11} ohms for 0.1 mf.; a correction was made for condenser resistance, the unknown being determined on the basis that the observed resistance was the resultant of the condenser and unknown resistances in parallel. This method was satisfactory provided the calomel electrodes serving as leads from the capillary were exactly isoelectric. Since this was not always the case and since we could not modify the equation to allow for this extraneous source of e.m.f. during the discharge we next turned to the other alternative, determining the rate of condenser charge through the unknown resistance. The e.m.f. of the unknown resistance, arising in the calomel electrodes, can be allowed for in this case. The charging e.m.f. can be either the stream potential of the capillary or an impressed e.m.f.; in either case the observed resistance of the capillary is the same. The resistance is expressed by the equation $R = \dfrac{-t}{2.303C \log (1 - V_t/V_f)}$, where V_t and V_f are the voltage at time t and the final or charging voltage, respectively. Here also the observed resistance is the resultant of unknown and condenser resistances in parallel. Since, however, the condenser is charged to only a fraction of the charging voltage, its leak becomes of much less importance than in the condenser discharge method. With the rate of charge method the error due to condenser leak is kept at a minimum because with low unknown resistances, i.e., below 5×10^9 ohms, the condenser resistance is so much higher than the unknown that its leak is negligible, while with high unknown the voltage at time t is usually only 20 to 35 per cent of the charging voltage so that relatively little opportunity for leak has

existed. However, it has seemed worth while to calculate the error due to condenser leak; when this has been less than 0.2 per cent it has been disregarded. The equation $R = \dfrac{-t}{2.303 \; KC \log \left(1 - V_t/KV_f\right)}$ has been derived independently and follows from equation 5, $q = \dfrac{r\,E\,C}{R+r} \left(1 - e^{-\frac{R+r}{R\,r\,C}\,t} \right)$, in the appendix of a paper by Bishop.[5] In our equation K is the correction factor $R_c/(R+R_c)$ where R_c is condenser resistance and R is the unknown resistance as first determined. A second approximation can be made by substituting
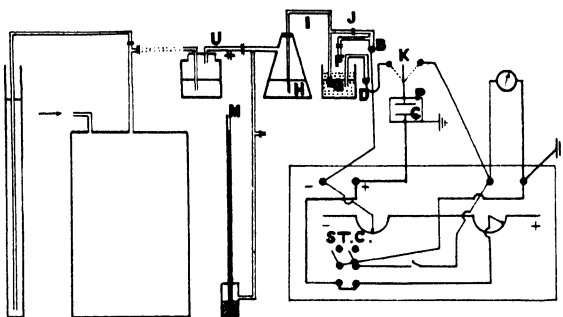
FIG. 1

for R in the correction factor the corrected R as found on the first approximation, but in any of our experiments the difference between the first and second approximations is hardly appreciable. In most of the determinations the first approximation introduces a correction of considerably less than 1/2 per cent; in only one case is it more than 3 per cent.

The final arrangement of apparatus is shown in Fig. 1; the potentiometric system has been modified from Bishop's arrangement[6] by substitution of a SPDT quick acting highly insulated switch for the tap key. With this one can determine either stream potential or resistance; the latter can be determined by utilizing either the stream potential or an impressed e.m.f. from the potentiometer.

The condenser C, the switch K, and that side of the high resistance source of unknown e.m.f. which is connected with the condenser are thoroughly insulated, the other side of the source of unknown e.m.f. is grounded at the galvanometer. Adequate insulation of the upper end of the capillary was uncertain because of the possibility of a leak to the flask H through the rubber tubing U; it was, however, a simple matter to insulate the lower end of the capillary, i.e., the beaker G and the electrode D. The condition was then fixed that the lead D would be connected with the condenser and since in the stream potential measurements this was always positive the battery current was reversed from the polarity marked on the box and was as indicated in the figure. The condenser C has been placed alternately upon a hard rubber table and upon a grounded sheet of galvanized iron P with no change in extent of charge from a known source of voltage; the

insulation of the condenser box is apparently adequate. When the potentiometer is set at zero and the electrodes are isoelectric there is no galvanometer deflection on the condenser discharge.

The steps of a resistance determination, using an impressed e.m.f., are as follows. The capillary holder I is put into the flask H which contains, in all of the experiments reported in this paper, 0.0005 N, 0.1 N or 1.0 N KCl. By proper manipulation of stopcocks a positive pressure of a few cm. Hg is applied and the tube F flushed out, cock J closed and tube F dipped into the beaker G, giving a low resistance circuit for the determination of electrode potentials. Calomel electrodes B and D are made up with 0.0005, 0.1 or 1.0 N KCl; they are usually 0 to 4 mv., occasionally as far as 10 mv. apart. The resistance of electrodes and connections exclusive of capillary is only 1.5 to 2.5 $\times$ 10^4 ohms with 0.0005 N KCl, i.e., practically zero as compared with the capillary resistances of 10^9 to 10^{11} ohms. The same proportion of course obtains with the concentrated solutions. This is of great importance as it enables us to disregard the resistance of the connections, which McBain could not do. The heights of the columns of solution in the right and the left arms of the capillary holder are next measured and their difference taken. This difference represents the negative pressure in the glass which will suck solution from the beaker up into the capillary. Since some evaporation from the beaker cannot be avoided, although it is freshly filled for each experiment, we next adjust the positive pressure, as indicated by the mercury manometer M, so that it just overtops the negative pressure, leaving a net positive pressure of 1 or 2 mm. Hg in the flask. This adjustment of pressure was occasionally checked as follows. If we have a net positive pressure of a few millimeters of mercury we can calculate the resultant stream potential, with 0.0005 N KCl, as about 1.5 mv. per mm. The algebraic sum of this and of the electrode potentials as determined through the low resistance circuit gives the potential which should exist across the capillary. When this is measured it always agrees with the calculated value.

Knowing the potential difference of electrodes exclusive of an impressed e.m.f. we next impress from the potentiometer an appropriate voltage, the total e.m.f. being the algebraic sum of the pre-existing and the impressed e.m.f. From 1000 to 1500 mv. with 0.1 mf. condenser were used with 0.0005 N KCl; from 100 to 200 mv. with 1 mf. with 0.1 or 1.0 N KCl. With some of the larger capillaries and 1.0 N KCl the measurements were made with a Wheatstone bridge. The charging time with the switch K to the left was taken with a stop watch, the ballistic throw of the galvanometer being observed when the condenser was discharged by throwing the switch to the right at time t. In no case was the time short enough that its measurement introduced an appreciable error. From 4 to 8 consecutive determinations were made on a capillary and their average taken as the resistance for that experiment; the variation of the corrected values of these consecutive determinations was practically always less than 1/2 per cent and never more than 1 per cent.

The observed values were corrected to a temperature of 25°C. by the equation $R_{25} = \dfrac{R_t}{1 - 0.022\,(t-25)}$. Within the comparatively narrow range of temperatures in these experiments the correction factor 0.022 remains almost constant. The beaker G was at room temperature, a thermometer was immersed in the beaker at the same depth as and close to the capillary and was read every few minutes. The capillary was completely immersed; the column of fluid in the capillary will almost instantly come to the temperature of the beaker; there is, indeed, no reason why the temperatures should differ to any significant extent.

A single figure for the resistance values given in Table I represents the average of a series of consecutive determinations, each determination being corrected for temperature and for condenser leak, when the latter is of significance. Other figures for the same capillary represent averages of similar series made at different times. After the final arrangement of apparatus had been perfected the results were surprisingly reproducible; no observed data have been rejected in the compilation of these tables except in a few instances where obvious sources of error, as partial obstruction of the capillary or an error in dilution of the solution, had entered. In these cases the source of error was proved by other objective means as by microscopic examination of the capillary or refractometric examination of the solution.

TABLE I

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	Observed / Calculated with 0.0005 N KCl
60	1.8	5.10	6.83×10^8 6.82×10^8	8.88×10^{10} 8.65×10^{10} 9.07×10^{10}	1.18×10^{11}		.752
61	.76	5.34	2.66×10^8 2.63×10^8 2.65×10^8	3.63×10^{10} 3.69×10^{10} 3.66×10^{10}	4.59×10^{10}		.798
64	1.25	5.64	3.92×10^8 3.87×10^8	5.60×10^{10} 5.43×10^{10} 5.59×10^{10} 5.64×10^{10} 5.37×10^{10}	6.75×10^{10}		.819
63	.75	5.76	2.26×10^8 2.27×10^8	3.39×10^{10} 3.30×10^{10} 3.33×10^{10}	3.93×10^{10}		.85
60a	.94	5.48	3.06×10^5 3.11×10^8 3.11×10^8	4.38×10^{10} 4.46×10^{10} 4.39×10^{10}	5.36×10^{10}		.823

TABLE I (Continued)

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	Observed/Calculated with 0.0005 N KCl
56	1.40	8.0	2.49×10^7		3.20×10^{10}	3.76×10^{10}	.88
			2.50×10^7		3.22×10^{10}		
					3.33×10^{10}		
					3.47×10^{10}		
					3.35×10^{10}		
66	.54	11.4		4.13×10^7	6.70×10^9	7.16×10^9	.933
				4.12×10^7	6.70×10^9		
					6.75×10^9		
					6.59×10^9		
					6.76×10^9		
					6.59×10^9		
					6.64×10^9		
65	.89	12.0		6.12×10^7	9.65×10^9	1.06×10^{10}	.926
				6.14×10^7	9.93×10^9		
					9.97×10^9		
					9.76×10^9		
					9.74×10^9		
					1.01×10^{10}		
30	1.60	25.6	2.77×10^6	2.41×10^7	4.00×10^9	4.17×10^9	.948
			2.73×10^6	2.41×10^7	3.94×10^9		
			2.76×10^6		3.92×10^9		
					3.95×10^9		
57a	1.97	39.0	1.446×10^6	1.26×10^7	2.19×10^9	2.17×10^9	1.00
			1.43×10^6	1.27×10^7	2.14×10^9		
					2.17×10^9		
57	4.45	39.4	3.27×10^6		4.94×10^9	4.94×10^9	.996
			3.27×10^6		5.08×10^9		
					4.84×10^9		
					4.83×10^9		
					4.85×10^9		
					4.96×10^9		
57b	2.48	39.7	1.803×10^6	1.59×10^7	2.61×10^9	2.72×10^9	.981
			1.805×10^6	1.60×10^7	2.66×10^9		
			1.807×10^6	1.59×10^7	2.66×10^9		
			1.806×10^6		2.73×10^9		
					2.71×10^9		
					2.67×10^9		
					2.67×10^9		
					2.65×10^9		

TABLE I (Continued)

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	Observed / Calculated with 0.0005 N KCl
59	4.66	40.5	3.26×10^6	2.87×10^7	4.71×10^9	4.90×10^9	.967
			3.29×10^6	2.85×10^7	4.77×10^9		
			3.26×10^6	2.87×10^7	4.76×10^9		
			3.23×10^6		4.70×10^9		
			3.23×10^6				
			3.23×10^6				
			3.26×10^6				
58a	1.90	96.0	2.38×10^5		3.54×10^8	3.56×10^8	.992
			2.37×10^5		3.53×10^8		
			2.35×10^5		3.55×10^8		
			2.35×10^5		3.50×10^8		
					3.52×10^8		
					3.55×10^8		
58	4.77	96.4	5.87×10^5		8.76×10^8	8.86×10^8	.986
			5.85×10^5		8.72×10^8		
					8.68×10^8		
					8.81×10^8		
58b	2.85	97.6	3.40×10^5		5.07×10^8	5.13×10^8	.988
			3.39×10^5		5.06×10^8		
			3.41×10^5		5.02×10^8		
			3.41×10^5		5.14×10^8		
					5.07×10^8		
25	6.15	102.8	6.68×10^5		1.014×10^9	1.007×10^9	1.01
			6.65×10^5		1.026×10^9		
					1.020×10^9		
					1.010×10^9		
					1.014×10^9		
					1.015×10^9		
					1.020×10^9		
63a	.25	5.78		7.45×10^7	1.05×10^{10}	1.29×10^{10}	.814
				7.43×10^7	1.06×10^{10}		
					1.04×10^{10}		
64a	.33	5.22		1.20×10^8	1.70×10^{10}	2.085×10^{10}	.818
				1.20×10^8	1.71×10^{10}		
67	1.77	18.6		4.65×10^7	7.28×10^9	8.06×10^9	.908
				4.64×10^7	7.42×10^9		
					7.23×10^9		
					7.34×10^9		
68	.62	1.82		1.865×10^9	2.18×10^{11}	3.24×10^{11}	.686
					2.26×10^{11}		

In the same way the resistance determinations can be carried out, using stream potential of capillary instead of impressed e.m.f. In this case a pressure of 60 cm. Hg is applied, the stream potential determined and the potentiometer then set at zero. The current from the stream potential then charges the condenser through the capillary resistance from time t, the galvanometer deflection being measured as before. The observed capillary resistance is the same whether potentiometer or stream potential is the charging e.m.f. This fact is of great theoretical interest, as it shows, among other things, that the resistances of a column of liquid in motion and at rest are the same, that the relatively rapid passage of liquid does not alter those surface conditions which determine surface conductance and that the stream potential can be made to furnish a reasonable amount of current (a great deal more than is required for its own measurement by the null point potentiometer-condenser method) without being affected. The figures in Table I which were obtained by using stream potential as source of e.m.f. are italicized.

Table I is a summary of all the results obtained on 21 capillaries ranging from 0.00182 to 0.1028 mm. bore. The length is the measured length, the diameter is that calculated from the observed resistance with 0.1 or 1.0 N KCl. This method of calculating diameter is valid only if the observed resistance of capillary plus connections is identical, within the limits of measurements, with the calculated normal resistance of the capillary alone when concentrated solution is used. The practical identity of these two resistances depends upon three conditions, first, that the resistance of connections be negligible, second, that the surface conductance be negligible and, third, that the pinch effect be negligible. The truth of these three conditions has already been established in the preceding paper. Since we are interested in actual conductances we have seen no reason to correct, as McBain has done, for conductance of solvent; in any event the correction is negligible.

Since resistance of connections and pinch effect are always negligible and with a concentrated solution surface conductance is also negligible, the diameter of the capillary is calculated from the equation diameter $= 2 \sqrt{\dfrac{\rho\, l}{\pi R}}$ where ρ is specific volume resistance of solution (8.95 ohms for 1.0 N and 77.8 for 0.1 N KCl), l is length of capillary in cm. and R is observed resistance in ohms. The value so obtained is the mean diameter of the capillary and has been taken as a better measure of diameter than the microscopic measurements. Having established its dimensions one next calculates the normal volume resistance of the capillary filled with 0.0005 N KCl, the 6th column of Table I. The 7th column compares observed and calculated resistances with dilute solution and shows far less surface conductance than found by McBain and coworkers.

A further analysis of our results with 0.0005 N KCl is given in Table II and Fig. 2. The last column in Table II gives the specific surface conductance, κ_s, calculated for each capillary.[7] In Fig. 2 the distance of the line OD above the X axis designates C_v/C_v, representing 100 per cent of the

normal conductance. For large tubes there is no other significant conductance but as diameter decreases an increasing amount of surface conductance is added. The distance of the line OE above OD represents the ratio C_s/C_v for the capillary diameter designated on the X axis. The line OE is drawn through the experimental points, the number by each point designates the capillary. The distance of OE above the X axis at any given diameter
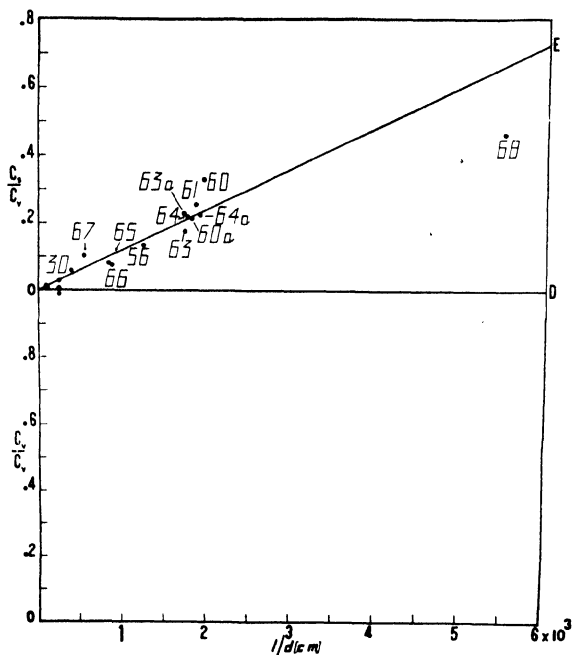
FIG. 2

represents $\dfrac{C_s + C_v}{C_v}$, the ratio of total or observed conductance to calculated or volume conductance; the reciprocals of these values coincide with the values in the 7th column of Table I.

It will be further noted that the slope of the line OE affords a method of calculating the mean specific surface conductance, κ_s, of all our experiments. $C_s = \kappa_s \dfrac{\pi\, d}{1}$ and $C_v = \kappa_v \dfrac{\pi\, d^2}{4l}$ where C_s and C_v are the surface and volume conductances, respectively, in mhos, of a capillary of length l and diameter d, and κ_s and κ_v are the specific surface and volume conductances. Then $C_s/C_v = 4\,\kappa_s/d\,\kappa_v$. This is of the form of the straight line equation $y = ax$, where $y = C_s/C_v$, $a = 4\,\kappa_s/\kappa_v$ and $x = 1/d$. Since then we are plotting C_s/C_v against $1/d$, the slope of the line is $4\,\kappa_s/\kappa_v$. The figure shows that the slope is $\dfrac{.242}{2 \times 10^3}$ or 1.21×10^{-4}. Therefore, $4\,\kappa_s/\kappa_v = 1.21 \times 10^{-4}$. But $\kappa_v = 7.41 \times 10^{-5}$, the normal specific conductance of 0.0005 N KCl. Therefore, $\kappa_s = 2.24 \times 10^{-9}$ mhos.

TABLE II

No.	Length (cm.)	Diam. (calc.) micra	R (observed) ohms	R_v (calc.) ohms	$R_s \left(\dfrac{R_v R}{R_v - R} \right)$ ohms	R_s/R_v	C_s/C_v	$\dfrac{1}{d\text{(cm.)}}$	$\left(C_s \dfrac{\kappa_s l}{\pi d} \right)$ mhos
60	1.8	5.10	8.87×10^{10}	1.18×10^{11}	3.57×10^{11}	3.03	.330	1.96×10^3	3.13×10^{-9}
61	.76	5.34	3.66×10^{10}	4.59×10^{10}	1.81×10^{11}	3.94	.254	1.87×10^3	2.52×10^{-9}
64	1.25	5.64	5.53×10^{10}	6.75×10^{10}	3.06×10^{11}	4.53	.221	1.77×10^3	2.31×10^{-9}
63	.75	5.76	3.34×10^{10}	3.93×10^{10}	2.23×10^{11}	5.67	.176	1.74×10^3	1.89×10^{-9}
60a	.94	5.48	4.41×10^{10}	5.36×10^{10}	2.49×10^{11}	4.64	.216	1.82×10^3	2.19×10^{-9}
56	1.40	8.0	3.31×10^{10}	3.76×10^{10}	2.76×10^{11}	7.34	.136	1.25×10^3	2.02×10^{-9}
66	.54	11.4	6.68×10^9	7.16×10^9	9.97×10^{10}	13.9	.072	$.877 \times 10^3$	1.52×10^{-9}
65	.89	12.0	9.84×10^9	1.06×10^{10}	1.37×10^{11}	12.9	.078	$.833 \times 10^3$	1.72×10^{-9}
30	1.60	25.6	3.95×10^9	4.17×10^9	7.50×10^{10}	18.0	.056	$.391 \times 10^3$	2.65×10^{-9}
57a	1.97	39.0	2.17×10^9	2.17×10^9	∞	∞	0	$.256 \times 10^3$	0
57	4.45	39.4	4.92×10^9	4.94×10^9	1.215×10^{12}	250	.004	$.254 \times 10^3$	indeterminate
57b	2.48	39.7	2.67×10^9	2.72×10^9	1.36×10^{11}	53	.019	$.252 \times 10^3$	1.39×10^{-9}
59	4.66	40.5	4.74×10^9	4.90×10^9	1.45×10^{11}	30	.033	$.247 \times 10^3$	2.53×10^{-9}
58a	1.90	96.0	3.53×10^8	3.56×10^8	4.19×10^{10}	120	.0083	$.104 \times 10^3$	1.52×10^{-9}
58	4.77	96.4	8.74×10^8	8.86×10^8	6.48×10^{10}	73	.013	$.104 \times 10^3$	2.46×10^{-9}
58b	2.85	97.6	5.07×10^8	5.13×10^8	4.34×10^{10}	85	.012	$.102 \times 10^3$	2.14×10^{-9}
25	6.15	102.8	1.017×10^9	1.007×10^9	indeterminate			$.097 \times 10^3$	indeterminate
63a	.25	5.78	1.05×10^{10}	1.29×10^{10}	5.65×10^{10}	4.38	.228	1.73×10^3	2.45×10^{-9}
64a	.33	5.22	1.795×10^{10}	2.085×10^{10}	9.36×10^{10}	4.49	.223	1.92×10^3	2.16×10^{-9}
67	1.77	18.6	7.32×10^9	8.06×10^9	7.97×10^{10}	9.90	.101	$.538 \times 10^3$	3.49×10^{-9}
68	.62	1.82	2.22×10^{11}	3.24×10^{11}	7.04×10^{11}	2.17	.462	5.50×10^3	1.55×10^{-9}

The arithmetic average of specific surface conductances obtained from all the capillaries of 0.025 mm. or less bore is 2.27×10^{-9} mhos. Obviously the results with the smaller capillaries, where the ratio of surface to volume is great, are the most dependable. The single 1.8μ capillary, no. 68, is probably an exception to this statement; technical difficulties increase rapidly as one gets below 5μ, which is about the optimum diameter for this work. With the 0.04 and 0.10 mm. capillaries the surface conductance is so small a fraction of the whole that its measurement involves a considerable error. Three of our 0.10 and 2 of our 0.04 mm. capillaries gave figures close to the average; the surface conductance with the others of these sizes is indeterminate. It must be remembered that with a 0.10 mm. capillary an error of 0.1 per cent in resistance determination gives an error of 10 per cent in specific surface conductance.

Discussion. McBain and Peaker found 13.0×10^{-8} mhos as the specific surface conductance with 0.001 N KCl and pyrex glass; this would have been not less than 1×10^{-7} for 0.0005 N KCl. As compared with their figure (our extrapolation) of 1×10^{-7} we find 2.24×10^{-9}, i.e., their figure for κ_s is 45 times as large as ours. We believe that the error of our methods of measurement is less than theirs; our ratio of surface to volume is many times as high, our cell resistance can be neglected and we had no "pinch effect." As a possible explanation of this great discrepancy in results we offer the suggestion that a large part of their observed increase in conductance was due to traces of chromic acid. The time effects described by McBain, Peaker and King might be explained on this basis. Our capillaries were cleaned by sucking hot water through them for an hour, followed in some cases by steaming for an hour; we found that the steaming process was probably not essential in conductance determinations. We did not use any cleaning solution and we have seen no change in capillary resistance with time.[8]

The increase of conductance with time in McBain's experiments might also be partly due to a liberation of electrolytes from the glass itself; when the ratio of surface to volume becomes high this factor is exaggerated, particularly with dilute solutions. The possibility of our solutions becoming more concentrated by the leaching of the glass surface was avoided by having a very slow continuous passage of solution through the capillary; in McBain's work the solution was stationary. The point might be raised that complete lack of relative motion between solution and glass surface is essential to the building up of a conducting layer. It seems unreasonable, however, that the forces of adsorption could be negatived by such a feeble agitation as was exhibited in our capillaries where the measurement was made by impressing an external source of e.m.f. In our work the resistance of a capillary was the same whether the solution was passing through it relatively rapidly under a pressure of 600 mm. Hg, the stream potential being used as a source of e.m.f., or whether the solution was moving at the extremely slow rate attained under a pressure of 1 or 2 mm. mercury. It seems only reasonable that if the movement of the solution past the glass surface disturbed the development of the conducting layer, this disturbance would be measurably greater when

the rate of movement was increased three hundred to six hundredfold. We are convinced that the state of a very slow exchange of solution is less open to objection than is no movement of solution. The suggestion that McBain's finding of a much higher specific surface conductance than ours may be due to the liberation of electrolytes from adsorbed chromic acid or from the glass itself is, of course, not capable of direct proof. The cause of the discrepancy may be some other source of error yet undetected. A discussion of some of the theoretical implications of these data with an extension of the work to include KCl solutions of other concentrations will appear in a later communication.

Summary

1.   An arrangement for determining either stream potential or resistance of pyrex capillaries filled with salt solution is described. Resistances up to 2.22×10^{11} ohms are measured by the rate of condenser charge method. Evidence is presented that polarization is avoided.

2.   There is no change of resistance with time.

3.   Capillaries of from 0.00182 to 0.10 mm. bore were used, macroscopic surface to volume ratios as high as 22,000 to 1 being obtained as compared with 1600 to 1 by McBain, Peaker and King.

4.   A specific surface conductance for pyrex glass and 0.0005 N KCl of 2.24×10^{-9} mhos was found, as compared with an extrapolated value of 1×10^{-7} by McBain, Peaker and King, their figure being 45 times as great as ours.

5.   The suggestion is made that the conductance figures of McBain and coworkers may be erroneously high because of contamination of solution by chromic acid or by leaching out of electrolytes from the glass. The possibility of this occurrence has been avoided in our work.

Bibliography and Footnotes

[1] McBain, Peaker and King: J. Am. Chem. Soc., **51**, 3294 (1929).

[2] McBain and Peaker: J. Phys. Chem., **34**, 1033 (1930).

[3] White, Urban and Krick: J. Phys. Chem., **36**, 120 (1932).

[4] Van Atta: Rev. Sci. Instr., **1**, 687 (1930).

[5] Bishop: Am. J. Physiol., **85**, 417 (1928).

[6] Bishop: Proc. Soc. Exp. Biol. Med., **27**, 260 (1930).

[7] Specific surface conductance is calculated by either of the following expressions. $\kappa_s = C_s l / \pi d$, where κ_s is specific surface conductance, C_s, l and d are the surface conductance in mhos, the length in cm. and the diameter in cm. of a capillary. C_s is the reciprocal of the 6th column in Table II. $\kappa_s = \dfrac{(R_v - R) \kappa_v}{R \times \text{ratio} \dfrac{\text{surface}}{\text{volume}}}$, where R_v is the calculated or volume resistance in ohms of a capillary, R the observed resistance and κ_v the normal or volume specific conductance. The ratio $\dfrac{\text{surface}}{\text{volume}}$ for a capillary is $\dfrac{40,000}{d}$, where d is the diameter in micra.

[8] Since these data were obtained and this paper written, further work on conductance in the smallest capillaries, both with 5×10^{-4} molar and with other concentrations of KCl, has not shown exact reproducibility with the same consistency as obtained in this series. Whether or not this is due to an artefact we are not yet prepared to state.

VISCOSITY OF THE SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

Prasad and Hattiangadi[1] have shown that when solutions of sodium silicate and of acids (or acidic ammonium acetate) are mixed together, crystalloidal silicic acid first formed goes over to the colloidal state and then follows the coagulation of the colloid solution by the electrolytes present in the mixture. Prakash and Dhar[2] have shown that the viscosity measurements of the jelly-forming mixtures reveal (1) the passage of the crystalloidal substance into colloidal state (2) the gradual neutralisation of the charge on the colloidal micelles (3) the formation of the specific structure of jellies. The present investigation was undertaken with a view to distinguish these three stages in the process of formation of the silicic acid gels.

The viscosity of silicic acid sols with and without the addition of electrolytes has been measured by Dhar and Chakravarty[3] who find that with increasing quantities of the electrolytes the viscosity of the sol at first falls, then rises to a maximum and again falls. Dhar[4] concludes that the degree of hydration and the viscosity of the sol increase as the charge on the colloidal particles is decreased. Thus it appears that the viscosity measurements of a colloidal system undergoing coagulation can also be utilised to measure the degree of hydration of the colloidal particles.

Experimental

Scarpa's apparatus[5] modified by Farrow[6] has been adopted with the following changes: (i) the connection of the guard tube opening the viscometer cylinder to the atmosphere has been kept at the top of the ground-glass stopper and not inside the cylinder thus ensuring constancy of the concentration of the solution under investigation (ii) ground-glass stoppers have been substituted for the wooden and rubber corks used by Scarpa and Farrow.

The viscometer with the guard tube is enclosed in an electrically heated air thermostat maintained at 40°C within ± 0.02°C.

The dimensions of the viscometer used are:

(i) Volume of the bulb between the two fixed marks........3.17 c.c.

(ii) Diameter of the capillary.............................8.9 mm.

(iii) Length of the capillary................................7.5 cms.

[1] J. Indian Chem. Soc., 6, 893 (1929).
[2] J. Indian Chem. Soc., 6, 391 (1929).
[3] Kolloid-Z., 44, 225 (1928).
[4] J. Phys. Chem., 29, 1556 (1925).
[5] Gazz., 40, 271 (1910).
[6] J. Chem. Soc., 101, 341 (1912).

The viscometer bulb of a small volume was selected because the rate of increase of viscosity of the gel-forming mixtures with time was found to be very great at a later stage of gel-formation and hence a viscosity reading could be taken in as short a time as possible.

Solutions of sodium silicate and acetic acid were prepared as described in the previous communication.

The gel-forming mixtures were prepared by mixing equal volumes (20 c.c.) of sodium silicate and acetic acid solutions and the viscosity of the mixtures with (i) different silica content and (ii) different amounts of the acid was measured at different intervals of time till the gel set.

The time of rise "t_1" and the time of fall "t_2" were measured by an accurate stop-watch. Another stop-watch started at the time of mixing the gel-forming constituents indicated the time since mixing at which the time of rise and of fall were measured. The mean of the time at which the mixture was made to rise and that at which it reached the lower mark while falling, was taken to indicate the time "T" at which the viscosity reading of the mixture was taken.

TABLE I

A. Alkaline gel-forming mixtures
Silica content—4 per cent

C = 0.35N pH = 9.86		C = 0.36 N (pH = 9.74)		C = 0.37 N (pH = 9.03)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3' 26"	7929	5' 9"	8991	2' 42"	8736
9' 12"	8187	11' 35"	9274	6' 16"	9426
12' 7"	8271	16' 38"	9788	7' 44"	9924
25' 43"	9326	20' 21"	10360	14' 40"	13020
31' 9"	9965	26' 53"	11500	18' 52"	15630
50' 25"	12350	30' 21"	12150	21' 33"	18870
52' 0"	12670	40' 34"	14500	24' 25"	23200
56' 7"	13490	43' 0"	15090	27' 44"	32290
59' 54"	14460	56' 24"	20480	29' 53"	∞
70' 41"	16970	58' 50"	22000		
75' 41"	18270	71' 43"	30490		
78' 6"	19130	75' 33"	38420		
97' 18"	27790	78' 0"	∞		
100' 9"	30460				
103' 55"	34810				
108' 0"	39680				
114' 45"	53520				
119' 40"	∞				

TABLE I

B. Acidic gel-forming mixtures
Silica content—4 per cent

C = 0.50 N (pH = 5.4)		C = 0.55 N (pH = 5.28)		C = 0.60 N (pH = 5.19)		C = 0.65 N (pH = 5.11)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
4' 49"	8330	3' 7"	7702	5' 14"	7667	6' 46"	7767
6' 13"	8529	5' 40"	7617	14' 15"	7602	20' 21"	7789
10' 8"	10970	18' 48"	8007	19' 12"	7617	25' 49"	7929
11' 55"	13390	24' 5"	8636	41' 2"	9466	32' 53"	8307
14' 4"	19570	30' 56"	10390	50' 21"	11950	41' 7"	8945
16' 0"	∞	32' 29"	11190	53' 45"	13840	44' 36"	9371
		34' 8"	12200	55' 41"	15250	49' 36"	10150
		37' 45"	15360	60' 5"	21190	54' 41"	11160
		40' 3"	19280	62' 5"	28270	59' 8"	12730
		41' 50"	23390	64' 0"	∞	61' 25"	13690
		43' 11"	∞			70' 20"	20810
						73' 2"	26200
						74' 38"	31810
						76' 0"	∞

TABLE II

A: Alkaline gel-forming mixtures
Silica content—5 per cent

C = 0.40 N (pH = 9.97)		C = 0.41 N (pH = 9.86)		C = 0.43 N (pH = 9.74)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
8' 17"	9303	2' 29"	9588	3' 6"	11190
10' 37"	9561	6' 1"	10290	4' 45"	12620
24' 21"	11050	9' 6"	11160	6' 46"	15330
31' 54"	12070	12' 59"	12180	9' 7"	21210
39' 30"	12970	20' 50"	14960	10' 30"	26610
45' 22"	14100	22' 59"	15820	12' 10"	∞
53' 24"	15960	25' 16"	17410		
60' 44"	17970	35' 22"	30860		
63' 5"	18750	39' 50"	44510		
70' 42"	22500	42' 40"	∞		
76' 44"	26980				
80' 15"	29950				
87' 40"	39330				
93' 13"	51390				
97' 28"	63450				
101' 0"	∞				

From t_1 and t_2 (expressed in tenth of a second) the viscosity η is calculated from

$$\eta = \kappa \left(\frac{t_1 \, t_2}{t_1 + t_2} \right)_{s} \quad \ldots \ldots \ldots \ldots \text{(i)}$$

where $K = \eta_w \left(\dfrac{t_1 + t_2}{t_1 \, t_2} \right)_{w}$ the calibration data of the apparatus, obtained from pure distilled water.[1] Taking the value of η_w to be 0.006535 (c.g.s. units) at 40°C from Thorpe and Rodger's data[2] the value of K was found to be 7118.5×10^{-8}. The coefficient of viscosity of the various gel-forming mixtures was then calculated from (i) and the results are given in the following tables, in which c represents the concentration of acetic acid added. Curves in which viscosity is plotted against time have been drawn and one of the set is shown in Fig. 1.

TABLE II

B. Acidic gel-forming mixtures
Silica content—5 per cent

C = 0.65 N (pH = 5.3)		C = 0.70 N (pH = 5.2)		C = 0.75 N (pH = 5.15)		C = 0.80 N (pH = 5.1)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 1″	9665	3′ 6″	8999	2′ 58″	8806	3′ 18″	8869
6′ 10″	10750	8′ 47″	9620	6′ 4″	9126	8′ 48″	8855
8′ 2″	11980	13′ 33″	10600	19′ 38″	10970	13′ 6″	9133
9′ 55″	14160	16′ 53″	12260	23′ 3″	12480	20′ 42″	9965
12′ 13″	19950	18′ 47″	13680	26′ 54″	15430	26′ 38″	11040
13′ 30″	∞	20′ 16″	15980	29′ 2″	18340	29′ 52″	12060
		23′ 5″	20240	31′ 34″	24550	33′ 40″	13690
		24′ 32″	23750	34′ 16″	28720	35′ 34″	15130
		26′ 0″	∞	37′ 5″	∞	37′ 43″	17680
						40′ 15″	22190
						43′ 35″	34420
						45′ 50″	∞

Discussion of Results

It appears from the curves shown in Fig. 1 that the viscosity increases slowly for some time after mixing the gel-forming constituents and afterwards the rate of increase becomes very rapid. The slow increase in viscosity may be due to the formation of the colloidal particles in the gel-forming mixtures and the rapid increase may correspond to the neutralisation of charge and consequent increased hydration of the particles and to the formation of definite structures in gels. Curves plotted with logarithm of viscosity against time are not straight lines as found by Prakash and Dhar[3] but are continuous curves having nearly the same shape as those shown in Fig. 1.

[1] Cf. Scarpa: Loc. cit. and Farrow: Loc. cit.
[2] Phil. Trans., 185, A II, 397 (1894).
[3] Loc. cit.

The first portion of the viscosity curves for the acidic mixtures is less steep than that for the alkaline ones and this may indicate that the rate of formation of the colloidal particles in the former mixtures is slower than in the latter ones. Further, the steepness of the curves for the two types of mixtures beyond a certain point shows that the increase in the viscosity of the acidic
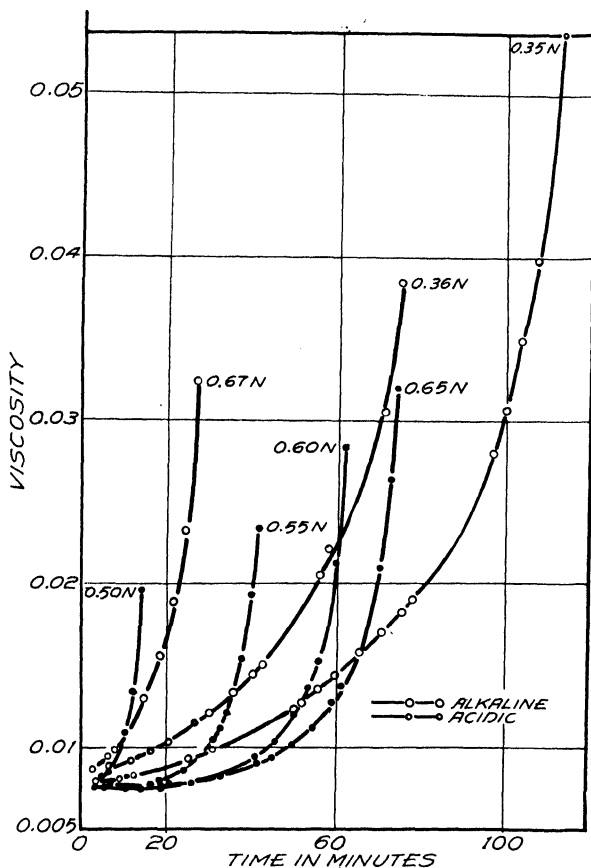
FIG. 1

Sodium silicate: 4%

mixtures is more rapid than that of the alkaline ones. This is probably due to the increased rate of hydration of the particles in the acidic mixtures.

Hatschek[1] has suggested that the viscosity of a colloidal system depends upon two factors (i) the volume of the disperse phase and (ii) the volume of the dispersion medium round each particle of the disperse phase. Dhar[2] has also pointed out that at constant concentration an increase in the degree of dispersion increases the hydration and the viscosity of the hydrophile colloids. From the extinction coefficient measurements the authors[3] have shown that

[1] Kolloidchem. Z., 12, 238-48 (1913).

[2] Loc. cit.

[3] Loc. cit.

the particles in the acidic mixtures are smaller in size than those in the alkaline ones. The increased rate of hydration of the particles in the acidic mixtures may, therefore, be due to the smallness of the particles in these mixtures. The greater hydration and the smaller size of the particles in the acidic mixtures than in the alkaline ones also explains the transparency of the acidic mixtures observed by Prasad and Hattiangàdi.[1]

It will be seen that with an increase in the H ion concentration of the mixtures the rate of increase of viscosity at first increases till a mixture setting in minimum time is reached and then slowly begins to decrease. This is due to the decrease in the density of the electric charge and consequent increase in the rate of hydration of the colloidal particles in alkaline mixtures and vice versa for the acidic ones.

The values of viscosity at the time beyond which further measurements are impossible are higher in alkaline mixtures than in acidic ones. This again points to the rapid increase in the hydration of the particles in the acidic mixtures, that is, indicates such a great increase in viscosity after the last point given in the curve that the next reading could not be taken. As the gels set in a much longer time than that for which the viscosity readings could be taken no information regarding the ultimate hydration of the particles can be obtained from these measurements.

Hatschek[2] has shown that the hydration factor of a colloid particle can be obtained from f/c where c is the concentration of the colloidal solution by weight and f, the ratio of the volume of the disperse phase to the total given by

$$f = \left(\frac{\eta' - \eta}{\eta'} \right)^3$$

where η_1 and η are the viscosities of the colloidal solution and the dispersion medium respectively. The values of f have been calculated from the first and the last readings of the viscosities given in the Tables I and II and are denoted by f_1 and f_2 in the following table in which C represents the concentration of acetic acid.

TABLE III

(a)   Conc. of SiO₂—4 per cent

C	0.35 N	0.36 N	0.37 N	0.50 N	0.55 N	0.60 N	0.65 N
$f_1 \times 10^3$	5.437	10.22	15.99	10.01	3.479	3.22	3.99
$f_2 \times 10^3$	676.4	571.9	507.5	295.6	374.2	454.6	501.9

(b)   Conc. of SiO₂—5 per cent

C	0.4 N	0.41 N	0.43 N	0.65 N	0.70 N	0.75 N	0.80 N
$f_1 \times 10^3$	26.35	32.26	72.04	33.95	20.52	17.15	18.24
$f_2 \times 10^3$	722.3	620.9	429.0	304.0	381.0	460.7	531.5

The above table gives an idea of the enormous change taking place in the hydration of the particles long before the gel has completely set.

[1] Loc. cit., p. 653.

[2] Kolloid-Z., **27**, 163 (1920).

Hatschek and Jane[1] have shown that the viscosity of the hydrophile sols and emulsions are directly related to their elasticity. It appears, therefore, from the results of viscosity measurements that the elasticity of the silicic acid particles considerably increases during the process of gel formation. The fundamental assumption made by Smoluchowski[2] in deriving a theory of the kinetics of coagulation is the complete inelasticity of the colloidal particles. The slight variations observed in the verification of the theory during a certain interval of gelation of silicic acid and the large variations at a later stage are probably due to the increased elasticity of the particles.

Summary

(1) Viscosity of silicic acid gel-forming mixtures has been measured with the progress of time by Scarpa's method as modified by Farrow and the time viscosity curves have been plotted.

(2) It is suggested that the slow rate of increase of viscosity during the preliminary stages of gelation is due to an increase in the number of colloidal particles. After a certain time the change in viscosity becomes fairly rapid: the rate of increase depends upon the size of the colloidal particles.

(3) The increase or decrease in the rate of change of viscosity on increasing the concentration of acetic acid in the alkaline or acidic mixtures has been explained on the relation between the charge on the colloidal particles and their hydration.

(4) The hydration factor has been calculated according to Hatschek's equation and it is shown that enormous changes in hydration take place during gelation.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

[1] Kolloid-Z., **39**, 300 (1926).
[2] Physik. Z., **17**, 557 (1916); Z. physik. Chem., **92**, 129 (1917).

INFLUENCE OF NON-ELECTROLYTES ON THE VISCOSITY OF SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

The sensitising and peptising influence of non-electrolytes is well known in the case of several colloidal solutions. Billitzer[1] found that a negatively charged platinum sol could be sensitised, discharged and charged positively by the addition of suitable amounts of alcohols. Klein[2] found that negatively charged sols of arsenious sulphide, silica, gold and ferric oxide are coagulated by alcohols, while positively charged sols of ferric oxide and silica are not affected. Prasad and Hattiangadi[3] while studying the effect of non-electrolytes on the setting of silicic acid gels found that the alcohols accelerate the gel-formation in the alkaline mixtures while they retard it in acid ones.

This behaviour of alcohols is explained on (i) the decrease in the dielectric constant of the mixture and (ii) the changes in the adsorbabilities of ions by the colloid particles.[4] Both these factors tend to bring about a change in the density of the charge of the particles. Mukherjee and Ghosh[5] have shown by cataphoretic experiments that the density of charge in the colloidal arsenious sulphide is decreased by the addition of alcohols. A change in the charge of the colloidal particles will cause a change in their degree of hydration as well as in the viscosity of the colloidal system.[6]

The present investigation deals with the influence of alcohols on the viscosity of the two types of gel-forming mixtures and was undertaken with a view to examine the changes in the hydration of the particles in the two types of silicic acid gels.

Experimental

10 cc. of acetic acid of double the concentration required for the experiment were mixed with a known amount of alcohol and the total volume was made to 20 cc. by diluting with distilled water. This solution was then mixed with 20 cc. of sodium silicate solution containing 4% silica prepared as described in the previous paper[7] and the mixture was immediately transferred to the viscometer. Viscosity measurements were then taken as described in the previous paper.[8]

pH value of the mixture in absence of alcohol was determined by mixing solutions of sodium silicate and acetic acid of required concentrations and using colorimetric method for the purpose.

[1] Z. physik. Chem., **45**, 312 (1903).
[2] Kolloid-Z., **29**, 247 (1921).
[3] J. Indian Chem. Soc., **6**, 991 (1929).
[4] Cf. Ostwald: "Grundriss der Kolloidchemie," p. 441; Mukherjee and collaborators: J. Indian Chem. Soc., **2**, 307 (1925); Weiser: J. Phys. Chem. 28, 1253 (1924).
[5] J. Indian Chem. Soc., **1**, 213 (1924).
[6] Cf. Dhar: J. Phys. Chem., **29**, 1556 (1925).
[7] J. Phys. Chem., **36**, 1384 (1932).
[8] Loc. cit.

In the following tables Q represents the cc. of alcohol in the mixture.

(a) The effect of ethyl alcohol in the alkaline mixtures.

The results obtained are given in Tables I and II and the time viscosity curves corresponding to Table I are shown in Fig. 1.

TABLE I

Acetic acid: 0.35 N
Reaction: Alkaline
pH: 9.86

Q : 0.0 cc.		0.5 cc.		1.0 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3' 26"	7929	2' 34"	9588	3' 17"	9840	3' 41"	11330
12' 7"	8271	7' 23"	9986	8' 10"	10760	5' 29"	11900
25' 43"	9326	15' 4"	10810	13' 15"	12280	7' 8"	13040
31' 9"	9965	22' 3"	11910	17' 27"	13930	8' 52"	14400
48' 30"	11990	27' 18"	12980	21' 25"	16350	15' 11"	22390
57' 54"	13780	31' 7"	13770	23' 36"	18380	19' 25"	48660
70' 41"	16970	35' 7"	14710	26' 5"	21830	22' 30"	∞
75' 41"	18270	40' 3"	16600	29' 9"	26540		
83' 7"	20870	44' 55"	19110	32' 35"	35370		
97' 18"	27790	50' 8"	22650	34' 45"	∞		
100' 9"	30460	53' 13"	25110				
108' 0"	39680	56' 26"	28310				
114' 45"	53520	60' 3"	33000				
119' 40"	∞	64' 3"	40550				
		70' 8"	73310				
		73' 50"	∞				

TABLE II

Acetic acid: 0.36 N
Reaction: Alkaline
pH: 9.74

Q : 0.0 cc.		0. 5 cc.		1.0 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^0$	T	$\eta \times 10^6$
5' 9"	8991	2' 49"	10490	4' 51"	11010	2' 51"	11000
11' 35"	9274	4' 25"	10650	6' 32"	11590	4' 28"	12130
13' 18"	9448	9' 19"	11150	8' 13"	12220	6' 17"	13590
16' 38"	9788	11' 3"	11740	10' 0"	12900	8' 24"	16090
20' 21"	10360	16' 52"	13730	11' 51"	14050	12' 36"	25480
26' 53"	11500	18' 49"	14680	13' 55"	15270	15' 10"	∞
30' 21"	12150	23' 0"	17040	16' 23"	17550		
43' 0"	15090	25' 20"	19130	18' 52"	20680		
50' 44"	17180	27' 55"	21900	21' 38"	25650		
53' 0"	19320	30' 57"	26130	25' 18"	38830		
56' 24"	20480	34' 30"	32600	27' 35"	∞		
71' 43"	30490	36' 41"	40310				
75' 53"	38420	38' 50"	∞				
78' 0"	∞						

Tables I and II and the curves in Fig. 1 show that ethyl alcohol exerts an accelerating influence on the rate of increase of viscosity of the alkaline gel-forming mixtures. This is in agreement with the observations of Prasad and and Hattiangadi.[1] It appears that the increased rate of viscosity is caused by the increased rate of hydration due to the decrease in the density of the charge of the particles brought about by the increasing amounts of alcohol.
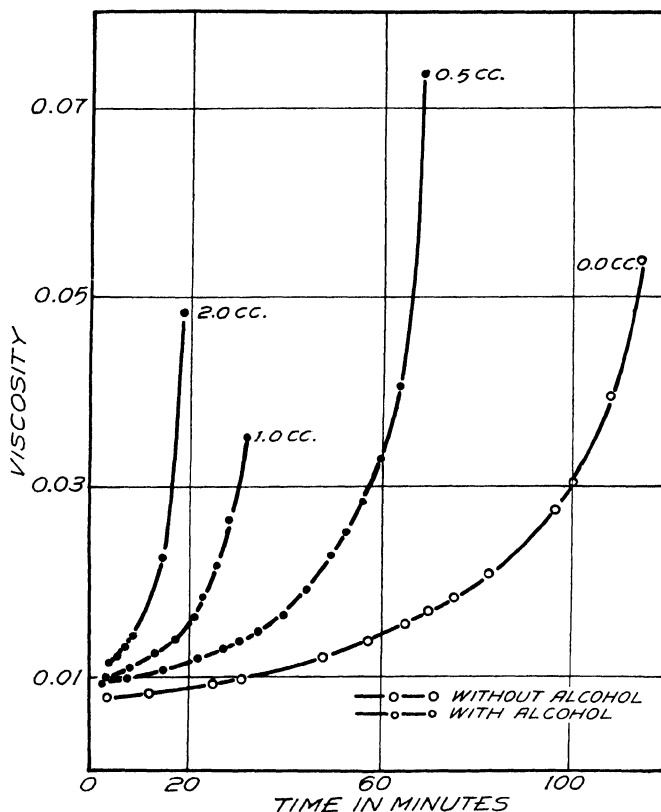
FIG. 1

Effect of alcohol on viscosity
Silica Content: 4%
Acetic acid: 0.35 N

On increasing the amount of ethyl alcohol beyond 2 cc. in the gel-forming mixture it is found that the mixture either sets instantaneously or a flocculent precipitate is obtained due to the low solubility of sodium silicate in alcohols.

(b)   The effect of ethyl alcohol in the acidic mixtures.

The results obtained are given in Tables III, IV and V and one set of time-viscosity curves is shown in Fig. 2.

[1] Loc. cit.

TABLE III
Acetic acid : 0.55 N
Reaction : Acidic
pH : 5.28

Q : 0.0 cc.		0.25 cc.		0.5 cc.		0.75 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3' 7"	7702	3' 9"	7530	5' 12"	7916	5' 3"	7683	3' 46"	8529
6' 56"	7580	11' 24"	7660	10' 55"	8200	13' 4"	8024	6' 37"	8559
9' 7"	7602	15' 12"	7902	14' 5"	8604	18' 33"	8399	9' 41"	8578
12' 48"	7638	17' 48"	8143	17' 2"	9177	21' 12"	8752	16' 48"	8806
16' 7"	7702	20' 18"	8429	18' 25"	9563	22' 34"	8913	19' 35"	8966
18' 48"	8007	21' 38"	8636	21' 15"	10480	24' 3"	9194	30' 57"	10960
21' 26"	8294	22' 58"	8855	23' 3"	11340	27' 5"	9908	34' 23"	12260
24' 5"	8636	24' 25"	9212	24' 49"	12470	28' 41"	10410	36' 4"	13140
27' 58"	9404	28' 9"	10470	26' 55"	14550	33' 29"	12720	38' 0"	14530
30' 56"	10390	29' 45"	11140	29' 7"	18000	35' 20"	14380	42' 21"	20550
32' 29"	11190	33' 14"	13750	30' 21"	21040	37' 28"	17210	45' 29"	32710
34' 8"	12200	35' 14"	16040	31' 40"	∞	40' 2"	23290	47' 30"	∞
35' 51"	13420	37' 36"	21460			41' 30"	∞		
37' 45"	15360	38' 23"	29770						
40' 3"	19280	39' 30"	∞						
41' 50"	23390								
43' 10"	∞								

TABLE IV

Acetic acid : 0.60 N
Reaction : Acidic
pH : 5.19

Q : 0.0 cc.		1.0 cc.		2.0 cc.		4.0 cc.		6.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
5' 14"	7667	3' 0"	9183	3' 49"	9419	5' 0"	8200	3' 21"	9665
6' 36"	7602	10' 24"	9333	12' 44"	9526	12' 13"	8565	9' 51"	9620
11' 51"	7580	13' 18"	9296	17' 17"	9759	16' 51"	8728	14' 36"	9752
14' 15"	7602	16' 5"	9376	26' 45"	10270	22' 51"	9397	17' 52"	9824
19' 12"	7617	20' 19"	9588	30' 0"	10400	27' 3"	9620	25' 37"	10100
41' 2"	9466	24' 50"	9888	33' 6"	10870	36' 2"	10210	30' 2"	10420
47' 18"	10850	28' 48"	10100	38' 6"	11800	39' 15"	10760	34' 6"	10640
50' 21"	11950	30' 48"	10350	43' 21"	13150	40' 44"	11090	38' 44"	11080
52' 0"	12730	37' 48"	11980	47' 48"	14950	42' 15"	11280	50' 3"	12520
53' 45"	13840	43' 15"	13770	51' 28"	16960	45' 44"	12000	53' 50"	13520
55' 41"	15250	45' 10"	14560	54' 31"	18910	49' 38"	12980	55' 51"	14080
60' 5"	21190	47' 9"	15690	57' 12"	21990	51' 52"	13730	58' 0"	**14700**
62' 5"	28270	49' 16"	17210	62' 1"	32700	53' 56"	14620	60' 0"	15310
64' 0"	α	51' 34"	19220	64' 0"	α	56' 2"	15520	61' 59"	16060
		54' 6"	22580			58' 27"	16880	64' 10"	17080
		57' 9"	29920			60' 51"	18880	69' 0"	20410
		59' 0"	α			63' 37"	21490	71' 49"	22980
						66' 30"	25630	74' 43"	26510
						69' 7"	35060	78' 0"	33060
						71' 20"	α	79' 58"	38700
								81' 0"	α

TABLE V

Acetic acid : 0.65 N
Reaction : Acidic
pH : 5.11

Q : 0.0 cc.		0.25 cc.		1.0 cc.		2.0 cc.		6.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^5$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3' 58"	7739	4' 58"	7502	4' 33"	7560	3' 27"	8570	4' 48"	9448
14' 39"	7702	10' 4"	7580	13' 11"	7721	12' 28"	8742	14' 31"	9590
23' 37"	7881	18' 54"	7602	19' 57"	7794	16' 12"	8756	19' 14"	9736
29' 33"	8132	31' 44"	7894	27' 26"	7923	20' 18"	8826	27' 52"	9895
34' 22"	8337	39' 18"	8429	32' 56"	8095	24' 48"	8849	32' 47"	9908
42' 57"	9124	53' 41"	10410	43' 37"	8642	27' 38"	9040	37' 31"	10140
51' 5"	10420	60' 41"	12160	51' 0"	9397	33' 25"	9177	42' 25"	10440
61' 25"	13690	64' 13"	13540	54' 32"	9951	39' 17"	9342	47' 5"	10530
70' 20"	20810	70' 45"	18280	59' 4"	10760	49' 32"	10040	53' 48"	10950
73' 2"	26200	73' 27"	21690	65' 33"	12460	52' 53"	10440	61' 15"	11770
74' 38"	31810	76' 45"	29890	69' 35"	14030	69' 1"	12730	68' 58"	12800
76' 0"	∞	78' 40"	∞	71' 36"	15080	74' 43"	14040	73' 35"	13580
				73' 47"	16580	79' 6"	15470	81' 30"	15360
				76' 1"	18430	81' 47"	16810	86' 15"	16960
				78' 31"	21400	86' 34"	19730	88' 31"	17760
				81' 17"	26310	91' 57"	24920	91' 3"	18810
				82' 54"	31060	95' 19"	29780	93' 32"	20260
				84' 30"	∞	102' 45"	63400	96' 10"	22250
						109' 5"	∞	102' 2"	27770
								105' 30"	33230
								110' 3"	47850
								115' 17"	91700
								120' 0"	∞

It appears that in moderately acidic mixtures (0.55 N and 0.60 N, Tables III and IV) quantities of alcohol less than 0.75 cc. accelerate the rate of increase of viscosity and quantities greater than this retard it; but in higher acidic mixtures (Table V) alcohols exert only a retarding influence. The latter observation is due to a decrease in the rate of hydration caused by an increase in the density of the charge of the colloidal particles. This is in agreement with
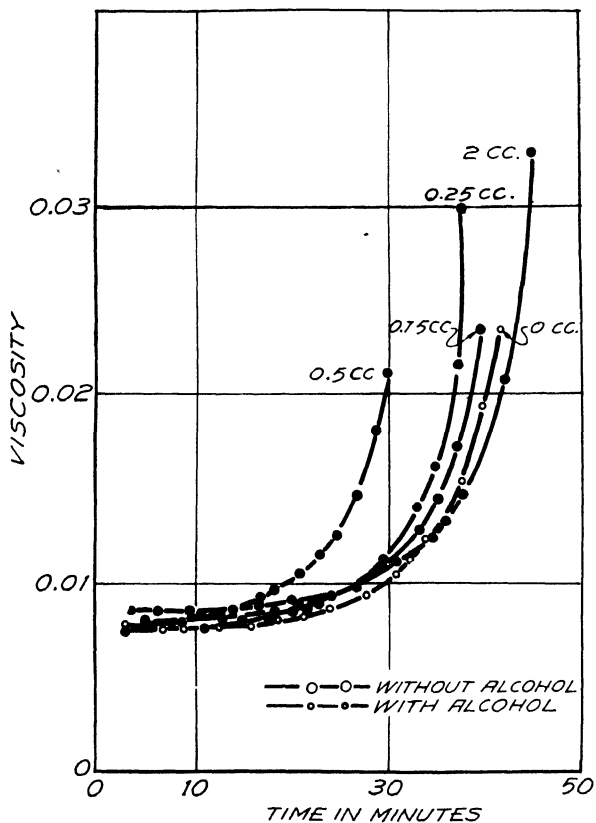
FIG. 2

Effect of alcohol on viscosity
Silica Content: 4%
Acetic acid: 0.55 N

the observations of Prasad and Hattiangadi[1] who found that in acidic mixtures alcohols act as protective agents.

The increase in the rate of viscosity in the presence of small amounts of alcohols in feebly acidic mixtures may be due to the decrease in the density of charge of the colloidal particles. This coagulating effect of alcohols even in acidic mixtures was not noticed by Prasad and Hattiangadi because they did not use such small amounts of alcohol as used in this investigation.

[1] Loc. cit.

It is evident that in moderately acidic mixtures (0.55 N and 0.60 N Tables III and IV) the rate of increase of viscosity is accelerated by small quantities of ethyl alcohol and retarded by larger amounts. But in higher acidic mixtures (Table V) ethyl alcohol exerts only a retarding influence.

(c)   The comparative effect of alcohols in the alkaline and acidic mixtures.

The effect of methyl, ethyl and propyl alcohols has been studied and the results obtained are given in Table VI and VII.

TABLE VI

Acetic acid: 0.36 N
Reaction: Alkaline
pH: 9.74

Methyl alcohol 1.0 cc.		Propyl alcohol 1.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$
3' 50"	8450	4' 15"	9164
7' 46"	9319	5' 40"	9482
15' 7"	12000	7' 15"	10040
16' 48"	12980	10' 19"	11290
20' 25"	15680	11' 53"	12130
24' 50"	21950	13' 34"	13220
27' 44"	30920	17' 36"	17850
30' 21"	48400	20' 6"	23100
33' 15"	∞	22' 40"	29020
		25' 5"	∞

TABLE VII

Acetic acid: 0.60 N
Reaction: Acidic
pH: 5.2

Methyl alcohol 1.0 cc.		Propyl alcohol 1.0 cc.		Methyl alcohol 4.0 cc.		Propyl alcohol 4.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
4' 19"	7647	6' 51"	7865	4' 45"	8450	7' 12"	9596
5' 42"	7650	12' 26"	7830	15' 37"	8468	16' 40"	9610
9' 26"	7617	17' 58"	7916	18' 57"	8549	21' 38"	9716
30' 29"	8770	23' 23"	8112	25' 13"	8910	38' 19"	11040
34' 44"	9354	31' 42"	8892	31' 11"	9333	40' 20"	11420
42' 16"	11240	35' 55"	9419	45' 43"	11920	44' 8"	12000
43' 53"	12010	38' 56"	10040	53' 29"	15440	49' 49"	13500
45' 31"	12770	41' 56"	10790	55' 34"	17120	53' 48"	15010
47' 17"	13710	45' 8"	11940	57' 50"	19500	55' 48"	16040
49' 6"	15240	52' 25"	17150	60' 32"	23240	59' 23"	17690
51' 9"	17470	57' 56"	28680	63' 48"	32450	60' 46"	19320
53' 29"	21230	59' 44"	∞	66' 55"	∞	63' '15"	22040
56' 52"	35670					66' 7"	26360
60' 0"	∞					69' 45"	37590
						72' 24"	∞

The time-viscosity curves are shown in Fig. 3 and for the sake of comparison the curves for the same mixture without the addition of alcohol and with 1.0 cc. of ethyl alcohol are also drawn in the same figure.
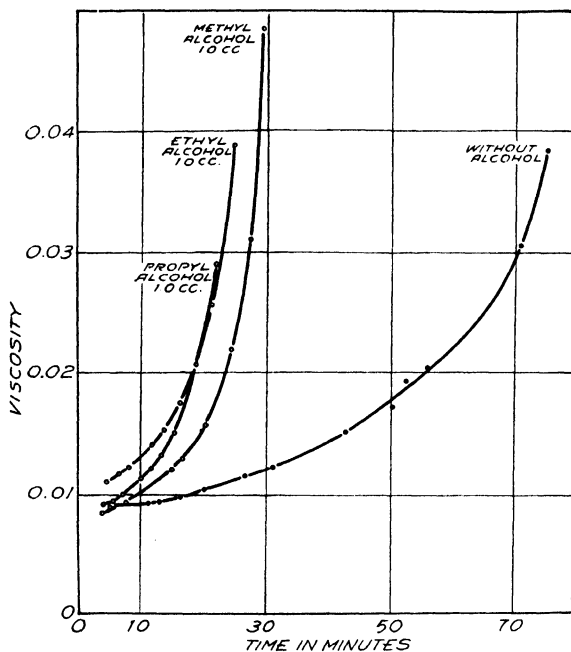
FIG. 3

Effect of alcohols on viscosity
Silica Content: 4%
Acetic acid: 0.36 N

The time-viscosity curves are shown in Fig. 4 and the two corresponding curves with ethyl alcohol and one without alcohol (Table IV) are also drawn in the same figure for the sake of comparison.

It will be seen that in the presence of alcohols the rate of increase of viscosity and hence the hydration is

(i)   increased in alkaline medium and the order of the effect of alcohols is

$$C_3H_7OH > C_2H_5OH > CH_3OH$$
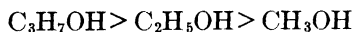
(ii)   increased in moderately acidic medium when small quantities of alcohols are added. The order of this influence is the reverse of the previous one, that is $$CH_3OH > C_2H_5OH > C_3H_7OH$$

(iii)   decreased (a) in highly acidic medium (b) in moderately acidic medium when the amount of alcohols added is great. The order of the alcohols is the same as in the alkaline medium, that is,

$$C_3H_7OH > C_2H_5OH > CH_3OH$$
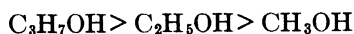
The order of the influence of alcohols in the alkaline medium is the same as that found by Prasad and Hattiangadi[1] on the time of setting of these gels.

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[1] Loc. cit.
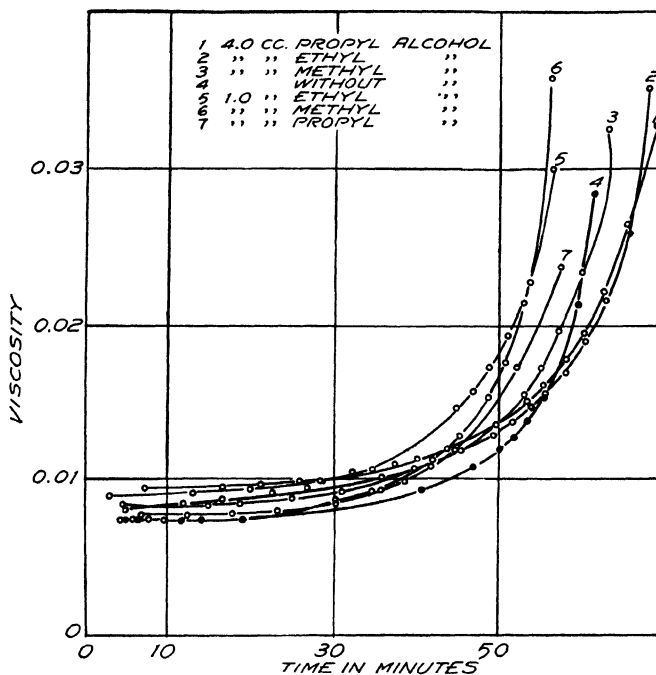
FIG. 4

Effect of alcohols on viscosity
Silica Content: 4%
Acetic acid: 0.60 N

The peculiar behaviour of non-electrolytes in sensitising the colloidal silicic acid particles in alkaline mixtures and protecting those in acidic ones cannot be explained on one single theory. Chaudhary[1] has pointed out that besides diminishing the dielectric constant of the system and changing the adsorbabilities of ions by the colloid particles, the non-electrolytes may also change the cohesive forces operative in a colloidal system. It will be interesting to carry out the charge measurements in the presence of alcohols under the various circumstances mentioned above and to see that the changes in the density of charge take place in the manner assumed above.

Summary

    The influence of alcohols on the viscosity of the silicic acid gel-forming mixtures has been studied by Scarpa's method as modified by Farrow and the accelerating influence of alcohols on the rate of increase of viscosity in alkaline mixtures as well as in moderately acidic ones (within a very small range of the alcohol added) has been explained on the assumption of the diminution in the dielectric constant of the mixture. The retarding influence of the alcohols in acidic mixtures, however, still remains unexplained.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

[1] J. Phys. Chem., **32**, 480 (1928).

SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS. I

BY E. LESTER SMITH

It is well known that phenol and cresol are more soluble in soap solutions than in water; advantage is taken of this phenomenon in the preparation of disinfecting solutions (e.g. Liquor Cresol Saponatus B.P., Liquor Cresol Glycerinatus B.P.C.) and it has formed the subject of several researches. Cyclohexanol and certain hydrocarbons have been incorporated with soaps to enhance their detergent action. It does not seem to be realised, however, that the solvent power of soap solutions is by no means restricted to these substances but is perfectly general. Every organic liquid that has been investigated is many times more soluble in soap solution (e.g. 10% sodium oleate), than in water; these solvated soap solutions differ greatly among themselves in their viscosity, foaming power, and the stability of their emulsions with excess of the organic liquid. The mixture of sterols, alcohols, hydrocarbons, etc., constituting the unsaponifiable fraction of most natural oils, though quite insoluble in water must obviously be soluble in soap solution, since soaps prepared from such oils yield clear aqueous solutions unless the unsaponifiable content is excessive. Moreover this unsaponifiable matter is retained by the soap with considerable tenacity against the competing solvent effect of extracting solvents, which also vary considerably among themselves in their effectiveness for extracting the unsaponifiable matter.

Although some of these facts are mentioned without comment in papers dealing with the estimation of unsaponifiable matter, they have hitherto excited curiously little interest, despite their evident bearing on a number of problems in theoretical and practical chemistry.

The present series of communications may be regarded as an attempt to map out this field, to link up and extend the few investigations on record and to relate the whole to our knowledge of the nature of aqueous soap solutions.

Review of Previous Publications

Pickering[1] observed the highly interesting fact that soap solutions can not only *emulsify* oils, but can actually *dissolve* considerable proportions of oil under suitable conditions. It appears that a certain soap manufacturer noticed that oils (presumably glyceridic) were soluble in soap solutions, and communicated the observations to Pickering, who extended it to mineral oils. Benzene and various paraffin oils were mixed intimately with potassium stearate or palmitate (in the form of 50% paste with water), the mixture was then diluted considerably with water, and the amounts of oil dissolved and emulsified, were determined after the emulsions had creamed. The soap would dissolve its own weight or more of oil, and retain it on dilution with water, but less oil was dissolved if the soap was diluted before mixing with the oil.

[1] J. Chem. Soc., 1917 III, 86.

Fischer[1] measured the "gelatin capacity" of a series of pure soaps for water, alcohol, and various organic liquids, i.e. the amount of liquid which could be held by 1 mol of the soap as a gel showing no syneresis. The entirely different physical states of gel and curd were however not clearly distinguished in this work.[2]

Bailey[3] describes the following system: water, phenol, sodium oleate at 20°, 40° and 60°; water, cresol, sodium oleate at 20°. The data are plotted in the manner usual for ternary systems, i.e. in equilateral triangles. The curves are of the binodal type which Bancroft has shown to be typical of systems of two partially miscible liquids and a third consolute liquid.[4]

The phenolic substance is completely miscible with soap solutions above a certain concentration.

Jenčič[5] has studied the solubility of cresols in soap solutions of the acetic series, in order to determine the minimum of soap necessary to give a homogeneous solution with a mixture of equal parts of water and cresol at ordinary temperatures, and also (ibid. 168) the minimum soap concentrations at which soap cresol mixtures yield gels.

Weichherz[6] in a study of xylol-water emulsions stabilised by soap (sodium oleate) found that concentrated soap solutions yield water-in-oil emulsions provided the phase-volume ratio is within a certain range, whereas dilute soap solutions yield in general oil-in-water emulsions: in the former case soap is dissolved in the xylol. Thus on adding water to a solution of soap in xylol a water-in-oil emulsion is first produced, which on addition of water beyond a critical phase volume ratio inverts to an oil in water emulsion. On account of the low solubility of sodium oleate in xylol, the work was extended by the addition of phenol to the system. The investigation of the quaternary system was limited to a study of the phase volume ratios and emulsion types produced by addition of water to an arbitrarily chosen mixture of xylol 79.94%, phenol 12.91%, and sodium oleate 7.15%. The mixture remained homogeneous up to a certain small water concentration, then further addition caused separation into two phases, the aqueous phase being small in volume, and forming unstable water-in-oil emulsions with the hydrocarbon phase; the aqueous phase decreased in volume as water was added, then disappeared, so that a second narrow homogeneous region appears on the diagram; still further additions of water again caused separation into two phases which formed relatively stable oil in water emulsions.

Three of the four ternary systems possible with the four components xylol, phenol, sodium oleate, water, were investigated, and also the variation of the viscosity of the quaternary system with increase of water concentra-

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[1] "Soaps and Proteins" (1921).
[2] See Laing and McBain: Kolloid-Z., 35, 18 (1924).
[3] J. Chem. Soc., 123, 2579 (1923).
[4] Bancroft: Phys. Rev., 3, 21 (1895); J. Phys. Chem., 1, 34 (1896); 1, 760 (1897); 3, 217 (1899); Proc. Am. Acad., 30, 324 (1894); Taylor: J. Phys. Chem., 1, 461, 542 (1897).
[5] Kolloid-Z., 42, 69 (1927).
[6] Kolloid-Z., 47, 133; 49, 158 (1929).

tion, and its behaviour at different temperatures. The findings could all be explained satisfactorily on the basis of the micelle theory of the structure of soap solutions developed by McBain. The author points out that it is not certain whether the solvents are adsorbed on the surfaces of the micelles, or whether any significant penetration or permeation occurs, but observes that the latter possibility is not unlikely.

More recently, Angelescu and Popescu[1] have studied in considerable detail the systems ortho-cresol, water, and the sodium potassium, ammonium, and lithium soaps of stearic, palmitic, and oleic acids, paying particular attention to the surface tension and viscosity of the solutions. Addition of o-cresol to sodium or potassium oleate solutions stronger than 0.1 N, causes at 20° first an increase in the viscosity to a maximum at about 2% cresol, then a decrease to a minimum at about 4% cresol, followed by a slow increase. With the palmitates, in general only a slow increase in viscosity occurs, similar to that which occurs with sodium hydroxide solution. The stearates are solid at 20° but at 40° to 50° behave similarly to the palmitates. The surface tension in most cases falls to a minimum for a small phenol concentration, then rises slowly. The solubility of o.-cresol in solutions of the three sodium soaps and in sodium hydroxide solutions was also measured. In the latter case a chemical reaction occurs, whereas in the case of the soap this possibility is excluded. Nevertheless, the solubility in the soap solutions is much greater than in the sodium hydroxide, particularly with the oleate and palmitate.

These results are explained on the micellar theory of the constitution of soap solutions. The maximum in the viscosity curve can probably be explained by Ostwald's hypothesis that, as the dispersion of a colloidal solution is increased, the viscosity passes through a maximum. Addition of cresol increases the dispersion of the colloidal particles until they almost reach the molecular state, corresponding to the minimum of the viscosity curve, whereupon further addition causes a slow increase as with sodium hydroxide or dilute soap solutions. This conclusion is substantiated by measurement of the specific conductivity of 0.2 N sodium oleate-cresol solutions, which passes through a maximum corresponding to the minimum viscosity, indicating that the soap is most fully dispersed at this stage. The authors conclude that the whole of the observations can be explained in a highly remarkable and satisfactory manner if it is assumed that the o.-cresol effects a reduction in the size of the colloidal soap particles, and that according to the theory of W. Ostwald a viscosity maximum occurs at a certain degree of dispersion.

It will be shown later that the results obtained in the present research (much of which was completed before the papers of Weichherz and of Angelescu and Popescu became available to the author) may be explained on very similar lines.

The author's interest in this subject was aroused by a technical research on which he was engaged, concerning the extraction of the unsaponifiable fraction from saponified fish liver oils, as a stage in the preparation of a con-

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[1] Kolloid-Z., **51**, 247, 536 (1930).

centrate of vitamins A and D. Besides the tendency of the soap solutions to emulsify almost all the solvents with which extraction was attempted, some quite unexpected problems arose. Among these were the high solubility of the solvents in soap solutions, the occurrence in some cases of systems of three liquid phases, and principally the surprisingly low partition coefficients for the unsaponifiable matter, between some solvents and soap solutions (saturated with the solvent.) The observation that the presence of alcohol in the system, besides rendering emulsions less stable, often increased the partition coefficient, did not render the problem less perplexing.

The small value of the partition coefficient with even the best solvents, such as ether, renders difficult the complete extraction of the unsaponifiable fraction. Tests of the published methods for estimating the total unsaponifiable matter of oils and fats showed that scarcely any of them give accurate results for this reason. In some cases, however, it was found that this source of error is partially compensated by failure to remove or estimate soap and fatty acid present in the extract. The details of this work have been published elsewhere.[1]

A few measurements of partition coefficients for vitamin A have also been published in a paper relating to a technique for the colorimetric estimation of this vitamin.[2]

Apart from the purely technical side, the present research has followed three main lines, which will form the subjects of this and subsequent papers.

1. Measurement of the solubility of a range of organic liquids in sodium oleate solutions, and observations on the salting-out of soap in the presence of organic liquids.

2. Measurements of partition coefficients for unsaponifiable matter, an azo dye and aniline between certain solvents and soap solutions saturated with the solvent.

3. Study of the phase equilibria in the quaternary system, sodium oleate, water, ethyl acetate, and sodium chloride.

Solubility of Organic Liquids in Sodium Oleate Solution

Experimental. Oleic acid was prepared from olive oil by the method described by Lawrence.[3] Sodium oleate was prepared in solution only, by heating the oleic acid with the calculated volume of standard sodium hydroxide (prepared from washed sticks and containing not more than 0.2% carbonate). Slight measured additions of oleic acid or soda were then made until a sample of the solution was just neutral to phenolphthalein on mixing with an equal volume of neutral ethyl alcohol. Laing and McBain[4] have shown that certain sodium oleate solutions can be obtained at room temperatures as sol, transparent jelly or opaque white curd. The preliminary experiments were

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[1] Analyst, **53**, 632 (1928).

[2] Biochem. J., **24**, 1942 (1930).

[3] "Soap Films."

[4] J. Chem. Soc., **117**, 1507 (1920).

made on a 0.4 N_w[1] solution, in the sol form. To a weighed quantity in a narrow-necked flask the organic liquid was added in small portions until a slight excess was present. Small additions of the soap solution were then made until the solution was just saturated with the organic liquid at 20°, becoming cloudy from separation of the latter at lower temperatures. No attempt was made to purify the solvents rigorously; in most cases they were taken from laboratory stock and redistilled, the fraction of correct boiling point being used. Accuracy was limited by the high viscosity of some of the solutions, the slowness with which some of the liquids dissolve, and the difficulty of detecting visually an excess of such liquids as ethyl ether, hexane, ethyl and methyl acetates, which yield almost transparent emulsions with the soap solution. The solubility of the liquids in water was also determined when no value could be found in the literature. In addition an emulsion of equal parts of the organic solvent and the saturated soap solution was prepared as follows, and its stability noted: to 5 ml of the soap solution in a test-tube was added 5 ml of the solvent in 1 ml portions, giving 20 vigorous shakes by hand after each addition, and an extra 20 shakes after the last. Some of the emulsions "broke" or "separated" in a short time, i.e. separated completely into two clear layers; others were "permanent" or "stable," i.e. the oil phase remained dispersed in globules for months, although in most cases "creaming" occurred, i.e. partial separation into aqueous phase and emulsion richer in the disperse phase. The mechanism of these phenomena is discussed in previous papers.[2]

Most of the organic liquids investigated show a perfectly definite solubility in the soap solution. At the saturation point the solution becomes cloudy on cooling and clears at the same temperature on warming slowly. This is not the case, however, with some solvents practically insoluble in water, such as anisol and the hydrocarbons. A certain proportion of such liquids can be dissolved by shaking and warming the 0.4 N_w soap solution with the liquid. A larger amount can however be "coaxed" into solution by other methods, for example by mixing the solvent into a stronger soap solution, which may be a curd initially, and then gradually adding water, or by mixing the solvent with oleic acid, stirring with the requisite amount of strong alkali (e.g. 2 N) and then diluting. The apparent solubility of these organic liquids in the soap solution varies with the manner in which the solution is prepared. For example if a mixture of equal weights of oleic acid and benzene is stirred with sufficient 2 N sodium hydroxide to neutralise the oleic acid, and the resulting gel of middle soap then diluted with water, a clear solution will result; neutralisation with $N/2$ alkali will on the other hand yield a cloudy solution. This is in line with the findings of Pickering.[3]

A value for the solubility in 0.4 N_w sodium oleate of a substance which behaved in this way was obtained as follows: oleic acid and the organic

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[1] 0.4 weight normal, i.e. 0.4 mols per kilo of water; 100 gm. contains 10.8 gm. sodium oleate.

[2] Quart. J. Pharm., **3**, 354, 362 (1930).

[3] Loc. cit.

liquid were weighed into a tube and the amount of 2 N sodium hydroxide necessary to neutralise the oleic acid stirred thoroughly into the mixture by means of a perforated plunger.

The resulting gel was then diluted gradually with sufficient water to make the soap 0.4 N_w. If the solution was clear, the experiment was repeated with increasing proportions of the organic liquid, until the solubility limit was reached, and the final solution appeared cloudy with excess of the liquid. The value obtained by this trial and error method does not necessarily represent the maximum solubility of the organic liquid in 0.4 N_w sodium oleate. In the case of benzene, however, which was studied in some detail, no greater amount could be got into solution, whether by the use of stronger or weaker sodium hydroxide solution to neutralise the mixture of benzene and oleic acid, by mixing the benzene with strong sodium oleate solution, or by using an excess of benzene and estimating the amount dissolved by methods similar to those used by Pickering.

Where two figures for solubility are recorded in the tables, the lower refers to the amount which can be dissolved directly by the 0.4 N_w solution, the higher to the value obtained by the above procedure.

TABLE I

Solubility of Aliphatic Compounds in 0.4 N_w Sodium Oleate Solution at 20°

Substance	Formula	100 gm. 0.4 N_w sodium oleate dissolves:	100 gm. water dissolves:	Stability of Emulsion
Hexane	C_6H_{14}	2.4 — 7.3 gm	Trace	Permanent
Chloroform	$CHCl_3$	20.6 gm	0.8[b] gm	,,
Carbon tetrachloride	CCl_4	6.65 gm	0.08[b] gm	,,
N butyl alcohol	C_4H_9OH	*Miscible* 0.2 N_w NaOH dissolves 59 gm	8.48[b] gm	Separated[c] in 4 mins.
Amyl alcohol[a]	$C_5H_{11}OH$	*Miscible* 0.2 N_w NaOH dissolves 58 gm	5.2 gm	Separated[c] in 4 mins.
Methyl acetate	CH_2COOCH_3	71 gm	32.0[b] gm	Separated in 1½ mins.
Ethyl acetate	$CH_3COOC_2H_5$	18.7 gm	8.6[b] gm	Separated in 10 mins.
Ethyl ether	$C_2H_5OC_2H_5$	20.6 gm	7.3[b] gm	Separated in 3½ hrs.
Paraldehyde	$(CH_3CHO)_3$	Not determined	11.6[b] gm	Separated in 10 mins.
Furfuraldehyde	C_4H_3OCHO	14.75 gm.	9.05[b] gm	Separated in 30 mins.

[a] Sharples Corporation's "Pentasol."
[b] Inter. Crit. Tables.
[c] Using 0.2 N_w sodium oleate.

Discussion of Results

The results obtained for aliphatic compounds or various types are shown in Table I, and for a series of mono-substitution products of benzene (including a few hydrogenated and di- and tri-substitution products) in Table II. At first sight there appears to be no rhyme or reason in the widely different solubilities and emulsifiabilities of these substances. For example, the extremes of complete miscibility and low solubility are exhibited by such closely related compounds as phenol and its methylation product, anisol. Substances of the same class behave quite differently. Among the esters for example, ethyl benzoate and amyl acetate yield permanent emulsions, while methyl and ethyl acetates yield emulsions which break in a few minutes.

TABLE II

Solubility of Aromatic Compounds in 0.4 N_w Sodium Oleate at 20°

Substance	Formula	100 gm. 0.4 N_w sodium oleate dissolves:	100 gm. water dissolves:	Stability of Emulsion
Benzene	C_6H_6	4.0 — 11.9 gm	0.15 gm[b]	Permanent
Toluene	$C_6H_5CH_3$	3.5 — 11.4 gm	Trace	Permanent
Nitrobenzene	$C_6H_5NO_2$	4.32 gm	0.19 gm[f]	Permanent
Aniline	$C_6H_5NH_2$	11.5 gm	3.62 gm[f]	Separated in 2 hrs.
p-Toluidine	$CH_3C_6H_4NH_2$	13.5 gm[a]	1.80 gm[af]	Permanent[a]
Phenol	C_6H_5OH	[e]Miscible 0.2 N_w NaOH dissolves 108 gm	8.93 gm[f]	Separated in 10 mins.[c]
o-Cresol	$CH_3C_6H_4OH$	37.6 gm[d]	2.87 gm[c]	Separated in 15 mins.
Thymol	$\frac{CH_3}{C_3H_7}\rangle C_6H_3OH$	2.0 — 6.3 gm[a]	0.08 gm[g]	Permanents[a]
Benzyl alcohol	$C_6H_5CH_2OH$	19.0 gm	3.8 gm	Separated in 15 mins.
Cyclohexanol	$C_6H_{11}OH$	59 gm	6 gm	Separated in 30 mins.
Ethyl benzoate	$C_6H_5COOC_2H_5$	5.4 gm	0.08 gm	Permanent
Anisol	$C_6H_5OCH_3$	2.1 — 7.2 gm	Trace	Permanent
Acetophenone	$C_6H_5COCH_3$	7.7	Trace	Stable. Separated in 14 days
Methyl cyclohexanone	$C_7H_{12}O$	22.5 gm	2.2 gm	Separated in 20 mins.
Benzaldehyde	C_6H_5CHO	5.8 gm	0.3 gm[f]	Permanent

[a] At 45°.
[b] Hill: J. Am. Chem. Soc., 45, 1143 (1923).
[c] Using 0.2 N_w sodium oleate.
[d] Angelescu & Popescu: Loc. cit.
[e] Bailey: Loc. cit.
[f] Inter. Crit. Tables.
[g] Fehling's, "Neues Handwörterbuch der Chemie."

Nevertheless, some striking relationships are revealed if the organic liquids are divided into two groups according to their solubility in water, taking as an arbitrary dividing line a solubility of about 2%. It then becomes evident that with few exceptions the liquids only slightly soluble in water have a solubility in the soap solution of under 10%; moreover they usually increase the viscosity of the solution and yield stable emulsions with the soap solution. On the contrary, liquids more soluble in water have a solubility in the soap solution of 10% or above, frequently decrease its viscosity, and yield unstable emulsions.

No other scheme of classification shows any such correlation; for example in Table III the organic substances are arranged in a manner calculated to

TABLE III

Stability of Emulsions of Organic Liquids in 0.4 N_w Sodium Oleate

Class of Compound	Emulsion unstable	Emulsion stable
Hydrocarbons		Hexane
		Benzene
		Toluene
		Xylene
Chlorinated hydrocarbons		Chloroform
		Carbon tetrachloride
		Ethylene dichloride
		Ethylene trichloride
		Ethyl bromide
Nitro compounds		Nitrobenzene
Amines	Aniline	[a]p-Toluidine
Phenols	[b]Phenol	[a]Thymol
	o-Cresol	
Alcohols	[b]N butyl alcohol	Caprylic alcohol
	[b]Isobutyl alcohol	
	[b]Amyl alcohol	
	Benzyl alcohol	
	Cyclohexanol	
Esters	Methyl acetate	Amyl acetate
	Ethyl acetate	Ethyl benzoate
Ethers	[a]Ethyl ether	Anisol
Ketones	Methyl cyclohexanone	[b]Acetophenone
Aldehydes	Furfuraldehyde	Benzaldehyde
	Paraldehyde	

[a] At 45°.
[b] Using 0.2 N_w sodium oleate.
[c] Required 3½ hours to separate.
[d] Separated in 14 days.

reveal any possible relation between type of compound and emulsifiability. A glance at the table shows that every substance which cannot be emulsified permanently by the soap solution is paralleled by another of the same class, often a homologue, which can be emulsified. The converse is however not true: no hydrocarbon or halogenated hydrocarbon has been found which cannot be emulsified.

It should perhaps be mentioned that previous studies of emulsification have not usually dealt with "oils" appreciably soluble in water, nor with such concentrated soap solutions. Solubility in water does not necessarily predispose to non-emulsifiability however; in the course of alkaloid assays on crude drugs, ether is often emulsified by the gums and saponins present; ethyl acetate can be permanently emulsified by gum acacia. With regard to the effect of soap concentration, Pickering[1] speaks of an *optimum* soap concentration for the emulsification of paraffin hydrocarbons; moreover, some of the liquids not emulsified by 0.4 N_w sodium oleate form more stable emulsions with dilute soap solutions.

Interpretation of Results

Previous workers have made some attempts to explain the high solubility of phenolic substances in soap solutions, but it appears to the author that two quite separate effects have hitherto been confused in such interpretations; namely, the effect of the colloidal soap in dissolving or adsorbing the organic liquid, and the effect of the latter on the degree of dispersion of the soap. McBain and his colleagues have given us an admirably clear picture of the nature of aqueous soap solutions, which is too familiar to need much elaboration here.[2] Neglecting the slight hydrolysis, a soap solution contains molecularly dispersed soap, sodium ions, simple fatty acid ions, colloidal aggregations of the latter (ionic micelles) and neutral soap micelles. More recent work[3] indicates that the two species of colloidal particle do in fact remain distinct from one another. The reversibility of equilibria in soap systems requires that every molecule comprising the colloid particles should be exposed to the liquid: the ionic micelle is pictured as "ten eels tied together by their tails" and the neutral colloid as a double layer of oriented molecules.[4] McBain has postulated that such a solution behaves towards external equilibria as a single phase. Nevertheless, for the present purpose it is essential to regard it as a two-phase system of hydrated colloidal soap particles (the two species not being differentiated) and a dispersion medium which is a dilute molecular solution of soap. Let us consider the behaviour of this system on addition of a substance such as cresol or ethyl acetate. The dispersion medium must dissolve the organic liquid to about the same extent as water, so that at the saturation point the dispersion medium becomes a saturated aqueous solution of the solvent; this

[1] J. Chem. Soc., **91**, 2001 (1907).

[2] See for example McBain and Salmon: J. Am. Chem. Soc., **42**, 426 (1920); McBain, Taylor and Laing: J. Chem. Soc., **121**, 621 (1922).

[3] Quick: J. Chem. Soc., **127**, 1401 (1925).

[4] McBain: J. Am. Chem. Soc., **50**, 1636 (1928).

alteration, like the addition of alcohol, is almost certain to affect the degree of dispersion of the soap—to render it "less colloidal" in fact. This term may cover a number of changes: more soap may pass into molecular solution: the average number of molecules per micelle may decrease: the hydration of the micelles may decrease: ionisation and hydrolysis, i.e. the ratio of ionic micelle to neutral colloid and acid soap, may be affected. Such changes are responsible for the variations in viscosity, surface tension, and conductivity, noted by Angelescu and Popescu[1] on the addition of o-cresol to soap. The rest of the organic liquid dissolved by the soap solution must, of necessity, be held in some fashion by the remaining colloidal soap particles. Whether it is adsorbed on their surface: whether (as Weichherz speculates) the solvent penetrates into the particles: or whether water of hydration is partially replaced by solvent molecules, must remain at present matters for speculation. Indeed, it may be doubted whether there is any essential difference between these possibilities, for if we accept McBain's conceptions of the micellar structures, then the particles become as it were "all outside," and there is no question of penetration into their interiors. Again, how definitely can one mark off a certain proportion of the water in the system as "bound" to the colloid as water of hydration?

An attempt to distinguish quantitatively between the molecularly dissolved and adsorbed solvent will form part of a later communication, but at this point one may draw attention to the very large amount of solvent adsorbed in proportion to the soap, in many cases. To take as an example the solubility of methyl acetate in $0.4 \, N_w$ sodium oleate solution; deducting the proportion dissolved by the water, it can be calculated that each gram of sodium oleate is responsible for the adsorption of about 3.6 gm of methyl acetate, or nearly 14 molecules of ester per molecule of soap. Allowing that part of the soap must be in molecular solution and thus ineffective, the true adsorption must be higher. This enormous adsorptive power may be compared with that of carbon, the most active preparations of which can adsorb rather less than their own weight of the most readily adsorbed solvents. The adsorptive power of sodium oleate for o-cresol and amyl alcohol is even greater, but it is less for other substances. These adsorption studies are also unique inasmuch as the adsorbent is a pure chemical substance in the form of a reversible colloid, the nature of which is fairly well understood; results are thus perfectly reproducible and independent of the mode of preparation of the adsorbent, but of course the latter cannot be separated from the aqueous menstrum (except by ultrafiltration).[2]

These considerations apply so far only to liquids which are appreciably soluble in water. But some liquids which are virtually insoluble in water are highly soluble in soap solution; such liquids must be held entirely by the colloidal soap particles. We might expect that equilibrium would not be attained so readily in these cases on shaking the soap solution with the organic

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[1] Loc. cit.

[2] See McBain and Jenkins: J. Chem. Soc., 121, 2325 (1922); McBain and Kistler: J. Phys. Chem., 35, 130 (1931).

liquid. In actual fact dissolution of such liquids in sodium oleate solution is often slow; the low rate of solution does not, however, appear adequate to explain the fact that in some cases the maximum solubility cannot be attained by shaking the soap solution directly with the organic liquid, but only by indirect means. Pickering[1] noticed this effect and suggested that once the liquid is emulsified, it is prevented from dissolving by protective films of soap surrounding the globules. Such an explanation does not accord well with modern theories of emulsification by soaps. One may perhaps suggest more reasonably that soap micelles which are already fully hydrated will not adsorb many molecules of a hydrocarbon (for example); in a strong soap solution, on the other hand, the micelles cannot be fully hydrated, but may if given the opportunity, adsorb hydrocarbon molecules to their maximum capacity, and on subsequent dilution retain the latter instead of taking up more water of hydration. In other words, we may suppose that a liquid such as phenol or ethyl acetate may easily displace water of hydration from a soap micelle, or itself be displaced thereby; whereas prior hydration of the micelle may prevent solvation with a non-polar liquid which has no affinity for water, and conversely prior solvation may prevent hydration on subsequent dilution with water; thus water and hydrocarbon, perhaps because they are attached to different parts of the soap molecule, are not mutually displaceable. Such a hypothesis is put forward only as a tentative suggestion at present especially since a curious phenomenon which was repeatedly observed with benzene throws some doubt on its validity. A soap solution containing nearly the saturation concentration of benzene (prepared by diluting a stronger solution to which the benzene had been added) remained perfectly clear on warming to 50° or 60°, and on *slowly* cooling again; but on cooling *rapidly* it became white and cloudy from separation of benzene. The solution cleared again almost immediately on warming, or on allowing to stand at room temperature it cleared in the course of an hour or so. The cycle of changes could be carried out repeatedly with the same solutions. The same phenomenon was observed with hexane.

We have seen that an organic liquid, which is appreciably soluble in water, is not only adsorbed by the colloidal particles of a soap solution, but by virtue of its solubility in the dispersion medium, it is likely to affect also the dispersion of the colloid. A liquid insoluble in water cannot have much effect on the degree of dispersion and nature of the colloid, since the dispersion medium remains unchanged, although the size of the particles must of course be increased by adsorption of large molecules of an organic liquid. It is evident from the data presented that it is this same factor, namely the presence or absence of the organic liquid dissolved in the dispersion medium, which controls the stability of emulsions of the liquid in question.

Bearing of Solvent Power of Soaps on Other Problems

The solvent action of soap solutions on oils has been almost entirely overlooked in connection with two problems on which it has an important bearing.

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[1] J. Chem. Soc., **111**, 86 (1917).

One of these is the mechanism of the saponification of oils by aqueous alkali. This is usually assumed to be purely an interface reaction, and the only function assigned to the soap formed is that of increasing the interface by its emulsifying action. It is now evident that the soap may play a more intimate part in the process by acting as a solvent for the oil; an investigation of the problem, which it is hoped to publish shortly, shows that this is indeed the case.

The other problem is the detergent action of soaps. Investigators have usually experimented either with solid dirt—carbon black, manganese dioxide, etc.,[1] or with oils or grease,[2] and seldom with both. Consequently different theories have been advanced, and while it is generally agreed that the solid dirt is peptised by the colloidal soap, grease is supposed only to be emulsified. Pickering[3] was the first to point out that soap solutions, particularly when concentrated, may actually dissolve oils, and he emphasised the consequent advantage of washing with concentrated soap solutions. Actually there is no real necessity to distinguish between the two types of dirt. The peptisation of solid dirt and the dissolution of oil are one and the same phenomenon, namely adsorption of the foreign matter by the colloidal soap particles in such fashion that in either case they pass through a filter. Similarly the suspension of excess of the solid dirt and the emulsification of excess oil are phenomena of the same nature. In each case particles of the foreign matter are temporarily suspended in the liquid in such fashion that they are retained by a filter, and, in course of time, settle or rise in the solution under the action of gravity.

Practical Applications of Solvent Power of Soaps

The most important application of soaps is of course their use as detergents, a function which is due in part to their solvent action on grease. Attempts have been made to increase their detergent value by incorporating cyclohexanol, benzene and other grease solvents into the soap, an operation which again owes its possibility to the solvent power of the soap for these substances. Another well-known example is the use of soap solutions to dissolve cresols to form concentrated disinfecting solutions which yield emulsions on dilution with water.

An ingenious application of this property of soaps to analytical chemistry has been described by Wilkie.[4] In determinations of the unsaponifiable fraction of waxes by extraction with ether from an aqueous solution of the saponified wax, the small solubility of the soap of the wax fatty acids is a source of trouble. Wilkie proposes to dissolve the wax in 9 times its weight of castor oil before proceeding with the analysis, applying finally a correction for the relatively small weight of unsaponifiable matter contributed by the castor oil. This method gives no trouble, because the castor oil soaps function as a solvent for the wax soaps.

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[1] See for example McBain, Harborne and King: J. Phys. Chem., 28, 1 (1924); also Fall: J. Phys. Chem., 31, 801 (1927).

[2] See for example Hillyer: J. Am. Chem. Soc., 25, 511 (1903).

[3] J. Chem. Soc., 111, 86 (1917).

[4] Analyst, 42, 200 (1917).

Soaps containing a small proportion of unsaponified oil dissolve to a clear solution in water. If alcohol is added the solvent power of the soap is reduced because it passes more completely into molecular solution, and the oil is thrown out of solution, rendering the liquid cloudy. This observation forms the basis of a delicate quantitative test for unsaponified oil in soaps or fatty acids, devised by the author.[1]

Salting-out in Soap-Solvent Systems

When salt is added to a soap solution containing an organic solvent, or when the soap concentration exceeds a limiting value, the soap is generally salted out, either as a solid curd or as a liquid layer; excess of the solvent may then constitute a third phase. A preliminary note on this subject has already been published[2] but further work has shown the existence of more types of equilibria than are there enumerated.

It is simplest to study these from the point of view of the addition of the solvent to a soap-water-salt system. The study of a number of such systems by McBain and his colleagues[3] has revealed the following types of salting-out:

1. $\begin{cases}\text{Isotropic solution (nigre).}\\ \text{Isotropic solution (lye).}\end{cases}$ 2. $\begin{cases}\text{Middle soap.}\\ \text{Isotropic solution.}\end{cases}$

3. $\begin{cases}\text{Neat soap.}\\ \text{Isotropic solution (nigre or lye).}\end{cases}$ 4. $\begin{cases}\text{Neat soap.}\\ \text{Middle soap.}\end{cases}$

5. $\begin{cases}\text{Curd soap.}\\ \text{Isotropic solution (nigre or lye).}\end{cases}$ 6. $\begin{cases}\text{Neat soap.}\\ \text{Middle soap.}\\ \text{Isotropic solution (nigre).}\end{cases}$

7. $\begin{cases}\text{Neat soap.}\\ \text{Isotropic solution (nigre).}\\ \text{Isotropic solution (lye).}\end{cases}$ 8. $\begin{cases}\text{Neat soap.}\\ \text{Isotropic solution (sat. lye).}\\ \text{Salt.}\end{cases}$

9. $\begin{cases}\text{Curd soap.}\\ \text{Neat soap.}\\ \text{Isotropic solution (lye).}\end{cases}$ 10. $\begin{cases}\text{Curd soap.}\\ \text{Isotropic solution (sat. lye).}\\ \text{Salt.}\end{cases}$

11. $\begin{cases}\text{Curd soap.}\\ \text{Neat soap.}\\ \text{Middle soap.}\\ \text{Isotropic solution}\end{cases}$ 12. $\begin{cases}\text{Curd soap.}\\ \text{Neat soap.}\\ \text{Isotropic solution (sat. lye).}\\ \text{Salt.}\end{cases}$

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[1] Analyst, **56**, 9 (1931).

[2] Nature, **127**, 91 (1931).

[3] McBain and Burnett: J. Chem. Soc., **121**, 1320 (1922); McBain and Langdon: **127**, 852 (1925); McBain and Elford: **1926**, 421; McBain and Pitter: **1926**, 893; McBain and Field: J. Phys. Chem., **30**, 1545 (1926); McBain, Lazarus and Pitter: Z. physik. Chem., **147**, 87 (1930).

All these "condensed systems" are also in equilibrium with the vapour phase which, however, will not be considered or counted as one of the phases. The three-phase systems are invariant in composition at an arbitrarily chosen temperature, while the four-phase systems can only exist at one definite temperature. We may expect any of these systems to persist on adding a small proportion of a solvent such as ethyl acetate. Larger additions may then destroy one of the phases, or if they all persist on saturation with the solvent, excess of the latter will constitute a new third, fourth, or fifth phase. The presence of vapour as an additional phase in equilibrium with the others is to be understood throughout. In addition, new equilibria may be introduced with the extra component. The following notes refer to a few of these possible systems which have already been realised.

In general, solvents seem to have a "liquefying" effect on the soap systems; this has been noted particularly with ethyl acetate and ethyl alcohol, but is probably fairly general. Thus a curd-lye system is often liquefied to isotropic solution, and so on. Acetone, on the contrary, has a dehydrating effect; it tends to precipitate curd from an isotropic solution.

A system which appears to correspond with the nigre-lye equilibrium is commonly observed in the extraction of unsaponifiable matter from soap solutions with ether, although only one reference to the phenomenon could be found in the literature.[1] When a considerable excess of alkali has been used for saponification, and when alcohol is also present, separation into three liquid layers often occurs. The lowest is alkaline lye, containing only a trace of soap: the middle is an isotropic soap solution, containing alcohol and much ether: the upper is ether, containing traces of water, alcohol and soap. The same phenomenon can be observed in many similar systems. A pair of solvents such as aniline and hexane, which themselves form a three-layer system with water, can be made to yield a four-layer system with soap solution and lye, as previously described.[2] In some cases in which the solvent is miscible with soap solutions above a certain concentration, salting-out yields a nigre-lye system in which the upper layer is completely miscible with the solvent, so that no third layer appears. This occurs for instance with sodium oleate and isobutyl alcohol, or sodium oleate and ethyl acetate above about 50°. Such systems may persist when the lye is saturated with salt so that solid salt may constitute a third phase. On the other hand, the three- and four-layer systems described above have not been observed in equilibrium with solid salt; similarly in the absence of organic solvent, the lye-nigre system only persists over a limited range of salt concentration in the lye.

Neat soap can exist in the presence of an excess of many organic liquids. This phenomenon permits the preparation of another series of three-layer systems—solvent, neat soap, isotropic solution (nigre or lye). Such systems must often have been produced unwittingly by the addition of salts to emulsions stabilised by soap, but appear to have been first observed by Wellman

[1] Archbutt and Deeley: "Lubrication and Lubricants," 320 (1927).
[2] Nature, **127**, 91 (1931).

and Tartar.[1] They found that on allowing a sodium stearate or palmitate solution to stand in contact with benzene at 25°, some of the soap was "transferred to the benzene phase in the form of a gel." A similar phenomenon occurred with sodium oleate and benzene on addition of salt. The effect was observed with 13 organic liquids. Systems in which such transference of soap occurred generally yielded water in oil emulsions on shaking. Wellman and Tartar did not clearly recognise the nature of this transferred soap, but some of the gels which they describe are in fact strongly anisotropic and may probably be classified as neat soap. This is particularly the case with sodium oleate salted out by sodium chloride in presence of such liquids as ether, chloroform and ethyl acetate. The "gels" obtained by spontaneous transfer of sodium stearate or palmitate to benzene or chloroform are, however, quite different in character, consisting apparently of masses of curd fibres enmeshing the organic liquid instead of water; they are formed presumably by virtue of the superior wetting power of the organic liquid for soap curd, and owe their translucency to a similarity in the refractive indices of the solid soap fibres and the liquid.

In the absence of solvents, neat soap does not exist in equilibrium with saturated lye and solid salt, except at high temperatures. In the presence of some solvents, however, such an equilibrium is possible at ordinary temperatures, giving the four-phase system solvent, neat soap, saturated lye, salt.

Salting-out to curd is also possible in the presence of excess of many solvents, giving rise to the system solvent, curd, isotropic solution (nigre or lye), which may also of course exist in the presence of solid salt as a fourth phase. There is obviously the theoretical possibility of a five-phase system—solvent, curd, neat soap, saturated lye, solid salt. In the four-component system constituted by a pure soap, an organic liquid, water and salt, five phases cannot coexist at an arbitrarily chosen pressure and temperature. By good fortune, however, such an equilibrium was actually observed in studying the system sodium oleate, sodium chloride, water and ethyl acetate. The quintuple point occurs in the neighbourhood of 25°, but is difficult to fix accurately, since it is not easy to establish equilibrium between five phases, one of which is a plastic gel.

In the absence of solvent, the system neat soap, nigre, lye, exists over a very narrow range of salt concentration. It should be possible to find an organic liquid which would coexist in equilibrium with these three phases, yielding another system of four liquid layers, but this phenomenon has not yet been observed.

There remain to discuss, the systems containing middle soap. It appears that this phase is less resistant to organic solvents than the other liquid crystal phase, neat soap. Sodium or potassium oleate in this condition will absorb a little ethyl acetate for example, but before the saturation point is reached, the middle soap breaks down to an emulsion, probably of neat soap and isotropic solution. Nevertheless middle soap appears to exist in equilibrium with solvents which are only slightly absorbed by the soap. These phenomena are

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[1] J. Phys. Chem., **34**, 379 (1930).

difficult to investigate, since middle soap forms a stiff plastic mass even in the presence of solvent, forming an ointment-like emulsion with excess of the latter. Moreover, although neat and middle soap can be readily distinguished from ordinary soap solutions, even when the latter are in the gel state, by examination under the polarising microscope, it is less easy to distinguish them from one another. One must be guided by the concentration ranges in which the two phases normally occur, by their different consistencies, and the fact that middle soap never exists in equilibrium with lye; but these properties are liable to be modified by the solvent.

Emulsions stabilised by Soap

The present studies have been concerned primarily with soap, and only incidentally with emulsions. Nevertheless, or perhaps for that very reason, they seem to throw a little light on the perplexing subject of the type and stability of emulsions, so that one may perhaps be pardoned for adding to the mass of literature on that subject. In most previous studies (of inversion by electrolytes for example), the soap has been, as it were, lost in an inseparable mixture of oil and water. Thus it has been almost impossible to discover anything about the condition of the soap—whether it is dissolved in the oil or water phase, or "adsorbed" at the interface: its hydration, solvation, and colloidal nature. Yet these things are obviously and admittedly the key to an understanding of the emulsion problem. Despite the large amount of work done in this field, the fact that sodium soaps are slightly soluble in hydrocarbons has only recently received mention in connection with emulsions[1] although several papers on the estimation of unsaponifiable matter refer to the fact. Similarly Wellman and Tartar even more recently have found that soap solutions may salt out in the presence of an organic liquid, transferring part of the soap to the latter phase, and that this condition can be correlated with the formation of water in oil emulsions on shaking. The work of Pickering seems to have received scant attention and no other investigator has mentioned the possibility of a transfer of organic liquid to the soap solution. The suggestion by Wellman and Tartar that the distribution of soap between the phases is the main type-determining factor marks an important advance, but in the light of the present work it seems possible to generalise still further. The following rules correlate emulsion type with the condition of the soap without reference to any theory of emulsification, and violence to any known experimental data.

    1. When the soap is in colloidal solution in the aqueous phase, it tends to stabilise oil in water emulsions.

    2. When the soap is salted out from the aqueous phase, it tends to stabilise water in oil emulsions.

    3. When the soap is partially salted out, it may stabilise either type of emulsion, depending on other conditions.

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[1] Weichherz: Kolloid-Z., **47**, 133; **49**, 158 (1929).

The term "salted-out" is here used in the widest possible sense, to cover removal of soap from solution in the aqueous phase, whether by increase in its own concentration, decrease of temperature, or addition of salts of the same or a different base, and irrespective of whether the salted out soap passes into solution in the oil phase, forms a third layer of isotropic or anisotropic solution, or appears as a solid curd insoluble in either phase; the emulsifying power of the soap in some of these conditions may be feeble.

The expression "tends to stabilise" has been used deliberately. It is not true for example that any relative volumes of oil and aqueous soap solution will yield a stable oil-in-water emulsion when shaken together. We have shown that some "oils" yield emulsions which exist for a few minutes or hours only. If the volume of oil greatly exceeds that of the soap solution, shaking may fail to subdivide the oil within the aqueous phase, although addition of the oil in small portions each followed by shaking may serve completely to emulsify the same volume of oil. It should be remembered that no pharmacist would ever prepare an emulsion (except a dilute emulsion of an essential oil) by simply shaking together all the ingredients. There is also a limit to the proportion of oil which a dilute soap solution can emulsify, though whether this is due to an approach to the limit of the specific emulsifying power of the soap, or to withdrawal of the soap into the oil layer (probably as acid soap) is not clear.

The emulsifying power of salted-out soap would appear to be feebler than that of soap in aqueous solution, since the water in oil emulsions are usually coarse. A finely dispersed and stable emulsion of this type can, however, be produced by stirring a natural glyceridic oil with strong aqueous alkali, as in the cold saponification process. A very low percentage of fatty acid in the oil will suffice (0.05%) and the emulsion must presumably be stabilised by minute particles of solid soap.

The most interesting emulsions are the third class, in which the soap is *partially* salted out. By focussing attention on the condition and phase distribution of the soap, rather than on its chemical nature, or on phase volume ratios, the phenomena of inversion receive a simple interpretation. The soap in the two conditions—aqueous solution and salted-out—must be regarded as having opposing or antagonistic emulsifying properties; it is as if there were two emulsifying agents present, stabilising, respectively, oil in water and water in oil emulsions, although in this case they may have the same chemical composition (or they may be soaps of different bases, e.g. Na and Ca). Evidently, when the soap is just beginning to salt out, the emulsion will probably be of the oil in water type; when it is almost completely salted out, it will probably be of the water-in-oil type. Between these two conditions it is not surprising that emulsions of either type can be prepared from the same mixture by different methods of shaking or mixing. The phenomenon is analogous to that observed by the author[1] when emulsifying cod-liver oil with the minimum of gum acacia. Exposure of this oil to the air causes slight oxida-

[1] Quart. J. Pharm., **3**, 373 (1930).

tion resulting in the formation of a trace of resin which stabilises water in oil emulsions. With care, an oil-in-water emulsion could be prepared, but too rapid addition of the oil caused inversion; this also occurred frequently on passing the emulsion through a homogenising machine. The phase-volume ratio, as emphasised by Weichherz[1] is not a primary type-determining factor, but sometimes appears to be so, because it determines the distribution of soap between the phases.

Summary

Organic liquids in general are much more soluble in soap solutions than in water.

Most liquids more soluble in water than about 2% have a definite solubility of 10% or over in 0.4 N_w aqueous sodium oleate at 20°, lower the viscosity of the solution and yield unstable emulsions with the soap solution.

Most liquids less soluble in water than about 2% have a solubility of less than 10% in 0.4 N sodium oleate at 20°, increase the viscosity of the solution, and yield stable emulsions with the soap solution.

This behaviour is general and independent of the chemical nature of the organic liquid.

Some liquids practically insoluble in water have a range of solubilities in this soap solution, depending on the method of preparation of the solution.

The phase equilibria possible in the four-component systems soap, water, salt, and an organic liquid are reviewed.

An attempt is made to correlate these phenomena with the detergent and emulsifying actions of soaps, and with present knowledge of the constitution of soap solutions.

Glaxo Research Laboratory, London, N. W. 1.
Research Laboratory, Chelsea Polytechnic, London, S. W. 3.
January 13, 1932.

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[1] Loc. cit.

THE COLLOIDAL SYSTEM, AGED HYDROUS ALUMINA-BASIC ALUMINUM CHLORIDE

BY H. V. TARTAR AND V. R. DAMERELL

Introduction

The preparation and study of colloidal hydrous alumina and ferric oxide have been the subject of many previous investigations. Two methods[1] of preparation have been used mostly, with some modifications. Solutions of salts have been boiled in which the acid produced by hydrolysis was volatile, and dialysis has been employed on salt solutions to which varying amounts of ammonia have been added, or none at all. The removal of the anion of the original salt, and of ammonia has been the difficulty in all of this work. Thus in the method of Neidle and Barab,[2] working with colloidal hydrous ferric oxide, the sols obtained had a ratio of equivalents of chlorine to aluminum of about 1 to 40. Bradfield,[3] by using a high-speed centrifuge, reduced this ratio to about 1 to 400.

The work presented herein received its impetus when it was found that hydrous alumina could be freed from anion by washing with dilute ammonia solution, after which practically all of the ammonia could be removed by further washing with distilled water. Using this method, sufficiently pure aged hydrous alumina could be obtained to warrant making *comparisons between the system disperse phase-peptizing solution and the peptizing solution alone*. This type of comparison was considered valuable as it enabled significant conclusions to be drawn regarding the behaviour of the disperse phase.

Aged hydrous alumina prepared in this way, even in its purest form, was in a colloidally dispersed state. It was found to be further stabilized, however, by the addition of various acids and salts. Basic aluminum chloride was found to act in this way, and for several reasons was chosen as the peptizing agent to be employed in this work. Thus equilibrium was reached much more rapidly than with hydrochloric acid, and an increase in acidity always resulted which served as a valuable indication of adsorptive power under various conditions.

Another phase of the work studied was the problem of reproducibility. The question of whether identical sols could be prepared starting from different materials, such as preparing the aged hydrous alumina from different aluminum salts, was considered important, and various attempts were made to settle this.

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[1] For a good bibliography of these methods see Weiser: "The Hydrous Oxides" (1926).

[2] J. Am. Chem. Soc., **39**, 80 (1917).

[3] J. Am. Chem. Soc., **44**, 965 (1929).

Experimental

Preparation of Aged Hydrous Alumina.

Hydrous alumina was prepared from the recrystallized chloride, nitrate and sulfate by precipitation with an excess of ammonia from cold solution. Varying amounts up to a pound of the salt in question were used, and the operation was carried out in a twelve-liter pyrex flask. The precipitate was washed by decantation, using a siphon, with distilled water for several weeks, a slight excess of ammonia being always kept present until a test portion showed that all of the anion of the original salt had been removed. Then it was washed without the addition of ammonia until it began to peptize, at which point it was centrifuged once for a short length of time in an International centrifuge No. 1 at 2500 r.p.m. and the hydroxide resuspended in distilled water by use of a shaking machine. This method yielded a colloid of great purity. None of the original anion could be detected by the usual tests on samples dissolved in acids. The ammonia content was found to be so low as to be essentially negligible. The determination was made by treating a known volume of the colloid with a large excess of solid sodium hydroxide, distilling into cold water, diluting the distillate to a known volume, and estimating the ammonia content by comparison with a known ammonia solution, using Nessler's reagent. Thus a sol prepared as above from the chloride gave a ratio of one equivalent of ammonia to 6000 equivalents of alumina. A sol prepared from the sulfate, washed and centrifuged a greater number of times, gave a ratio of one equivalent ammonia to 25000 equivalents of alumina.

Recent work by the junior author[1] has indicated that the aged hydrous alumina prepared in this manner is the hydrate $Al_2O_3.3\ H_2O$. X-ray work has indicated that it is definitely crystalline, being probably the hydrate bayerite. However, in view of the method of preparation the name aged hydrous alumina will be retained.

Preparation of Basic Aluminum Chloride Solutions.

Aluminum chloride, designated as chemically pure, was dissolved in distilled water (specific conductance 5×10^{-6} mhos), filtered and recrystallized without the addition of hydrochloric acid. Two stock solutions were made at different stages of the work from different amounts of recrystallized salt. Hereafter they will be referred to as solution A and B.

	Equivalents Aluminum per liter	Equivalents Chlorine per liter
Solution A	1.338	1.256
Solution B	0.2277	0.2166

These basic solutions, when treated with pure aged hydrous alumina showed the peculiar phenomenon of increasing in acidity. (See Tables I, II, III). This change is attributed largely to the adsorption of such ions as $Al(OH)^{++}$ or AlO^+, which would be expected to be present in greater amounts

[1] Damerell: J. Phys. Chem., **35**, 1061-7 (1931).

in the basic solutions than in solutions of the normal salt. Thus solution B, not so basic as solution A, did not show such a great increase in acidity when aged hydrous alumina was added. According to Heyrovsky,[1] the normal chloride gives no increase in acidity when treated with hydrous alumina.

Preparation of the Sols.

Sols were made by adding the pure aged hydrous alumina in distilled water to the basic aluminum chloride solutions. Sols prepared in this way were found to reach equilibrium in several days, as shown by tests with the hydrogen electrode. *Basic aluminum chloride solutions were used instead of hydrochloric acid because previous experiments showed that many months were necessary for sols peptized with the latter to come to equilibrium.*

Change of acidity of sols peptized with hydrochloric acid

Equivalents alumina/liter	Equivalents HCl/liter	pH after standing seven weeks	pH after standing one year
0.045	0.006	2.93	4.03
0.045	0.013	2.30	3.89

This fact makes it doubtful, in the systems of many other investigators who peptized their disperse phase with hydrochloric acid or other acids, *whether equilibrium was established at the time that their measurements were made.*

Hydrogen Ion Activity Measurements.

Hydrogen ion activity was determined with the hydrogen electrode, used in conjunction with a normal calomel half-cell. The hydrogen electrodes were prepared by a modified method of Clark described earlier.[2] At least two electrodes were used on each solution tested, and the potentials were required to check within a few tenths of a millivolt. Twentieth molar potassium acid phthalate solution was used as a buffer in testing the worthiness of the electrodes. It was consistently found that electrodes began to give low voltage readings after they had been used for some time in contact with the colloid. A type K Leeds and Northrup potentiometer and a wall galvanometer were used, and all voltage readings were taken with the cells in a thermostat kept at $25° \pm 0.03°$. Sörensen values were calculated from the formula:

$$pH = \frac{\text{Observed E.M.F.} - 0.2848}{0.05911}$$

(a) *Change in hydrogen ion activity of basic aluminum chloride solution with the addition of increasing amounts of aged hydrous alumina.* Aged hydrous alumina prepared from the sulfate was used. A stock sol, 2.025 normal, with respect to aluminum content, was prepared and diluted with varying amounts of water and basic aluminum chloride solution A to give a series

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[1] J. Chem. Soc., 117, 21 (1920).

[2] Damerell: J. Chem. Education, 7, 1664 (1930).

of six 250 cc. samples. They were allowed to stand for over a month, with occasional shaking, although experience showed that equilibrium was established in two or three days. The results are shown in Table I.

TABLE I

Change of acidity upon adding aged hydrous alumina
to basic aluminum chloride solutions

Equivalents of chlorine/liter from basic aluminum chloride	Equivalents of aged hydrous alumina/liter	pH
0.005	0.00	4.13
0.005	0.05	3.80
0.005	0.10	3.79
0.005	0.30	3.78
0.005	0.70	3.775
0.005	1.45	3.765

(b) *Change of acidity upon adding increasing amounts of basic aluminum chloride to aged hydrous alumina.* The aged hydrous alumina was prepared from the sulfate. Ten 250 cc. samples were made from the stock alumina sol and basic aluminum chloride solution A. These sols were allowed to stand a month with occasional shaking. A trace of potassium chloride was added to the first members of the series to increase conductivity since otherwise the galvanometer did not give satisfactory deflections. In Table II are shown these hydrogen ion activities, together with the activities of the same strength basic aluminum chloride solutions not containing the colloid.

TABLE II

Acidity of various basic aluminum chloride solutions with and without 0.05
equivalents of aged hydrous alumina per liter

Equivalents of chlorine/liter from basic aluminum chloride	pH of soln. alone	pH of soln. plus aged hydrous alumina
0.00	7.00	7.07
0.0005	—	4.26
0.001	4.455	4.06
0.005	4.15	3.78
0.01	4.03	3.685
0.02	3.93	3.655
0.05	3.76	3.605
0.07	3.705	3.605
0.10	3.62	3.575
0.20	—	3.48

(c) *Variation of acidity of basic aluminum chloride solution upon addition of equal amounts of aged hydrous alumina of different average particle size.* Alumina prepared from the nitrate was used here. A flask of the purified colloid dispersed in water was allowed to partially settle. Then portions

were taken from the top, middle and bottom, and each analyzed for alumina in the usual way. From the analyses, a sol was made up from each containing just 0.05 equivalents of alumina per liter of the sol. Enough basic aluminum chloride had also been added to make the final concentration of each sol 0.01 equivalents per liter. They were allowed to stand a week, and the hydrogen ion activity measured on each. As the results show in Table III, the smaller size particle caused the greater acidity.

TABLE III

Acidities of basic aluminum chloride solutions containing equal amounts of aged hydrous alumina of different average particle size

Equivalents of chlorine per liter from basic aluminum chloride	Equivalents of added alumina/liter	Average size of particle	pH
0.01	0.00	—	4.03
0.01	0.05	large	3.94
0.01	0.05	medium	3.87
0.01	0.05	small	3.825

(d) *Change of acidity upon settling.* Several sols containing varying amounts of alumina and basic aluminum chloride were allowed to settle, the pH of the top portion of the sol then being determined. As seen in Table IV, these activities are slightly different than those of the shaken up sol.

TABLE IV

Decrease of acidity upon settling

	pH of settled sol	pH of shaken up sol
Sol I	3.675	3.66
Sol II	3.735	3.72
Sol III	3.725	3.71

An explanation of this peculiar effect will be offered later.

(e) *Change of acidity upon precipitation with sodium sulfate.* The sodium sulfate was prepared by recrystallization and ignition, and the anhydrous salt used in all cases. To avoid any changes in equilibrium that might result from dilution, weighed amounts of the solid salt were used instead of solutions. For comparison, a duplicate series containing only basic aluminum chloride and sodium sulfate was prepared in one experiment, and the acidities determined. The difference obtained in the two cases could thus be attributed to the effect of the disperse phase. The results are given in Tables V and VI. The slight break in the pH curve, which can be observed much better in Graph I, seems to occur in all such precipitation curves. In some cases it was so small as to be within the limits of experimental error, while in other cases it was more noticeable, although never of great magnitude. (See Tables V, VI, VII, VIII, and IX.)
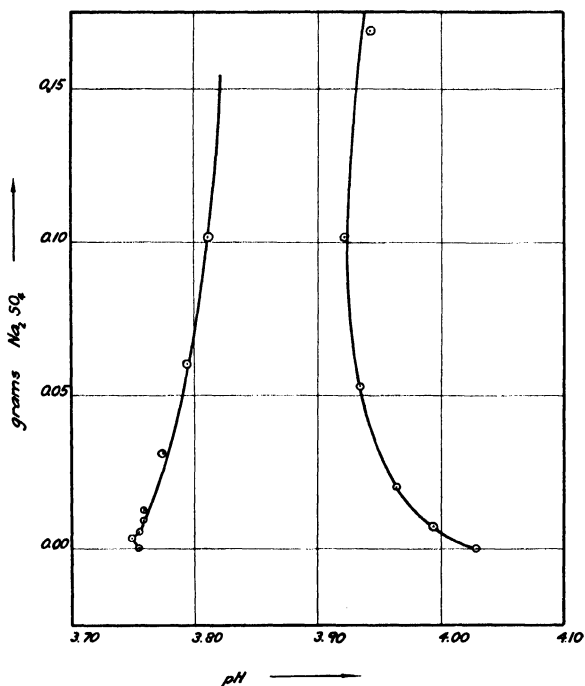
GRAPH I

Change of acidity with addition of sodium sulphate

TABLE V

Change of acidity upon adding increasing amounts of sodium sulfate to
colloidal aged hydrous alumina peptized with basic aluminum
chloride solution A.   (250 cc. samples were used)

Equivalents chlorine per liter from basic aluminum chloride	Equivalents aged hydrous alumina per liter	Grams sodium sulfate added	pH of mixture
0.012	0.0454	0.0000	3.78
0.012	0.0454	0.0010	3.76
0.012	0.0454	0.0034	3.755
0.012	0.0454	0.0058	3.75
0.012	0.0454	0.0088	3.73
0.012	0.0454	0.0106	3.75
0.012	0.0454	0.0138	3.765

(f) *Change of acidity upon precipitation with potassium chloride.* This
was conducted in a similar manner to (e). Potassium chloride was prepared
by recrystallization and ignition, and in all cases the solid salt was used, to
avoid errors that might result from dilution. Three series were run, one with
just basic aluminum chloride solution and two with basic aluminum chloride

TABLE VI

Change of acidity upon adding increasing amounts of sodium sulfate to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, with and without 0.05 equivalents/liter of aged hydrous alumina prepared from the chloride.   250 cc. samples taken

Grams of sodium sulfate	pH of solution plus alumina	pH of solution alone
0.0000	3.755	4.03
0.0035	3.750	
0.0052	3.755	
0.0075		3.995
0.0092	3.76	
0.0135	3.76	
0.0200		3.965
0.0312	3.775	
0.0535		3.935
0.0608	3.795	
0.102	3.81	3.92
0.17		3.94
0.24	3.835	3.95

solution plus aged hydrous alumina, prepared from the nitrate and chloride. The time required for the precipitation mixture to come to equilibrium was found by testing the first series at intervals to be in the neighborhood of three weeks. The last series was therefore allowed to stand a month before obtaining the hydrogen ion activities. The series containing just basic aluminum chloride and potassium chloride came to equilibrium much faster. The results are shown in Tables VIII and IX. A series of precipitations was also run using a mastic sol prepared by Tartar and Draves[1] in their work, to determine whether the small break in the hydrogen ion activity curve was able to be detected in this case at the precipitation point. Such an effect was noticed, but it is seen to be very small. The results are given in Table VII.

TABLE VII

Change of acidity upon adding increasing amounts of potassium chloride to mastic sol, containing 10 grams of mastic per liter of sol.
250 cc. samples were used

Grams of potassium chloride	pH
0.1	3.825
0.25	3.815
0.4	3.825
0.6	3.83
1.2	3.825
3.6	3.80

[1] J. Phys. Chem., **30**, 763 (1926).

TABLE VIII

Change of acidity upon adding increasing amounts of potassium chloride to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, and containing 0.045 equivalents of aged hydrous alumina from the nitrate. 200 cc. samples taken

Grams potassium chloride added	pH after 2 days	pH after 7 days	pH after 27 days
0.0	3.79	3.79	3.79
0.5	3.90	3.87	3.84
1.0	3.94	3.91	3.885
1.5	3.97	3.915	3.895
2.0	3.975	3.946	3.925
2.5	3.995	3.96	3.945
3.0	4.01	3.965	3.955

TABLE IX

Change of acidity after a month upon adding increasing amounts of potassium chloride to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, and containing 0.050 equivalents of aged hydrous alumina per liter prepared from the chloride, or containing no alumina. 250 cc. samples taken

Weight of potassium chloride in grams	pH of solution alone	pH of solution plus alumina
0.0	4.03	3.75
0.5	—	3.825
1.0	4.15	3.85
1.5	—	3.885
2.0	—	3.91
2.5	—	3.92
3.0	—	3.93
3.5	—	3.94
4.0	4.21	—
10.0	4.215	3.945
25.0	4.245	3.96

Chloride Ion Activity Measurements.

Chloride ion activities were measured in the usual way. A platinum wire sealed into a piece of glass tubing was immersed in mercury which in turn was covered with calomel, and the solution to be investigated was introduced over this after having been saturated with calomel. The half cell so prepared was allowed to stand for several hours, and then its potential was measured against a normal potassium chloride calomel half-cell, using a saturated potassium chloride bridge. With this method, essentially the same chloride ion activity was observed in basic aluminum chloride solutions with and without the colloid, when hydrous alumina that had aged for many months was

employed.   With hydrous alumina prepared for only a few weeks, however, a slight adsorption of chlorine apparently took place.   The results are given in Tables X and XI.

TABLE X

Voltage obtained when basic aluminum chloride solutions with and without aged hydrous alumina were saturated with calomel, put over mercury, and referred to a one normal potassium chloride calomel mercury half-cell at $25°$.

Alumina was prepared fourteen months previously from the sulfate

Stock solution of basic aluminum chloride	Equivalents/liter of chlorine from basic aluminum chloride	Equivalents/liter of aged hydrous alumina	Voltage
A	0.012	0.00	0.1075
	0.012	0.05	0.1080
B	0.010	0.00	0.1094
			0.1094
B	0.010	0.0102	0.1093
			0.1097
B	0.010	0.0297	0.1095
			0.1095
B	0.010	0.0481	0.1095
			0.1097

TABLE XI

Similar to Table X, except aged hydrous alumina had been prepared seven weeks previously from the chloride

Stock chloride solution	Equiv./liter Cl	Equiv./liter alumina	Voltage
B	0.010	0.00	0.1094
			0.1094
B	0.010	0.0112	0.1126
			0.1127
B	0.010	0.0300	0.1128
			0.1127

Conductance Measurements.

The specific conductance of the series containing increasing amounts of aged hydrous alumina was determined at $25°C$. and the results are given in Table XII.   The changes taking place here are brought out better in Graph II.   The specific conductance of the series containing a constant amount of aged hydrous alumina and increasing amounts of basic aluminum chloride is also given in Table XIII.
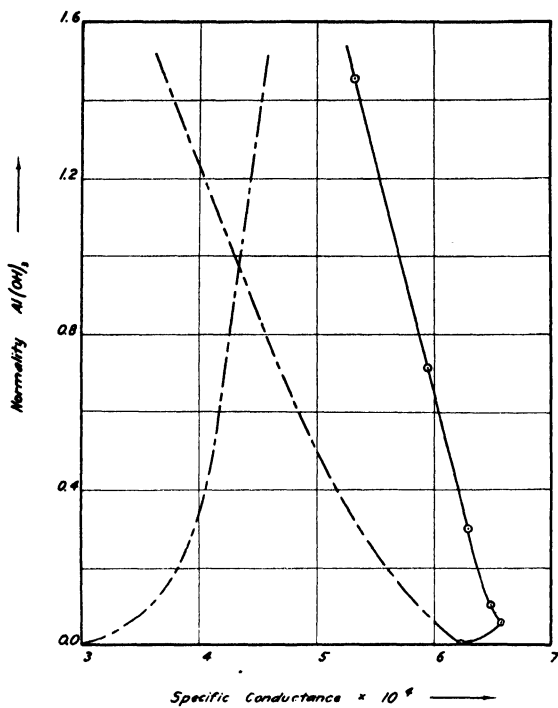
GRAPH II

Change of specific conductance with increasing amounts of aged hydrous alumina

TABLE XII

Conductance of basic aluminum chloride solution containing increasing amounts of aged hydrous alumina

Equivalents chlorine per liter from basic aluminum chloride	Equivalents per liter of aged hydrous alumina	Specific Conductance in mhos
0.005	0.00	0.0006215
0.005	0.05	0.0006578
0.005	0.10	0.0006501
0.005	0.30	0.0006274
0.005	0.70	0.0005943
0.005	1.45	0.0005315

Determination of Aluminum in True Solution by Difference.

It was desired to know, if possible, the composition of the intermicellular liquid, since a knowledge of this was necessary in order to compare it to the original basic aluminum chloride solution. Ultra-filtration could have been used, but it was decided that the chance of error was no greater in the following procedure, which was chosen because of greater simplicity.

TABLE XIII

Conductance of series containing a constant amount of aged hydrous alumina
and increasing amounts of basic aluminum chloride from
stock solution A at 25°C.

Equivalents chlorine per liter from basic aluminum chloride	Equivalents per liter of aged hydrous alumina	Specific Conductance in mhos
0.00	0.05	6.6×10^{-6}
0.0005	0.05	8.57×10^{-5}
0.001	0.05	1.6×10^{-4}
0.005	0.05	6.43×10^{-4}
0.01	0.05	1.19×10^{-3}
0.02	0.05	2.22×10^{-3}
0.05	0.05	4.98×10^{-3}
0.07	0.05	6.28×10^{-3}
0.10	0.05	8.98×10^{-3}
0.20	0.05	1.675×10^{-2}

Samples of the colloid were analyzed for total chlorine and total aluminum
in the usual gravimetric manner. Further samples of the same colloid were
treated with ammonium oxalate, and the colloid, which precipitated very
quickly, was filtered and washed repeatedly with distilled water. It was then
dried and ignited to constant weight in the usual way. Any adsorbed ammo-
nium oxalate would be expected to volatize with this treatment. By sub-
tracting the weight of aluminum oxide representing only the colloid from the
weight of aluminum oxide representing the total aluminum present, the
aluminum in solution was computed. This was compared to the total chlo-
rine, since electrometric measurements had indicated that there was essen-
tially no chloride ion adsorption, except by the hydrous alumina prepared
only a few weeks. It seems probable, from the results which are given in
Table XIV, that the electrolyte present in the intermicellular liquid corre-
sponded closely to normal aluminum chloride.

TABLE XIV

Analysis for aluminum in true solution

Grams colloidal aged hydrous alumina as Al_2O_3	Grams total aluminum as Al_2O_3	Grams Difference	Equivalents aluminum in true solution	Equivalents chlorine in true solution
(1) 0.0643	0.0761			0.0072
(2) 0.0648	0.0766			0.0073
Ave. 0.0645	0.0763	0.01180	0.00695	0.00725

*Attempt to reproduce Aged Hydrous Alumina Colloids starting with Different
Aluminum Salts.*

An extensive series of experiments was conducted in an attempt to pre-
pare a reproducible aged hydrous alumina colloid. The hydrous alumina
could not be peptized with hydrochloric acid because of the length of time

required to reach equilibrium. Using basic aluminum chloride as the peptizing agent many experiments were tried with sols of just the same composition in which the aged hydrous alumina was prepared from different salts. In all cases the results indicated that similar colloids did not result when the aged hydrous alumina was prepared from different sources. Thus in Table XV is given the hydrogen ion activities of two series of colloids, one series containing aged hydrous alumina prepared from the sulfate, the other containing aged hydrous alumina prepared from the chloride. They are seen to be dissimilar.

TABLE XV

Hydrogen ion activities of two series containing aged
hydrous alumina from different sources

Equivalents/liter of chlorine from basic aluminum chloride	Equivalents/liter of aged hydrous alumina	Source of aged hydrous alumina	pH
0.01	0.00	sulfate	3.82
0.01	0.0102	,,	3.75
0.01	0.0297	,,	3.685
0.01	0.0481	,,	3.67
0.01	0.00	chloride	3.82
0.01	0.0112	,,	3.77
0.01	0.0300	,,	3.75

It was thought that the two members of Table XV having a pH of 3.75 might have the same total surface, and to test this further, the minimal precipitation value was determined using potassium chloride. The break was difficult to determine, due to the very gradual variation in each precipitation series. The approximate amounts of potassium chloride necessary to precipitate 10 cc. of each was found to be

    Sol (3) of chloride series   0.15 grams
    Sol (2) of sulfate series   0.10 grams

Discussion of Results

The increase of acidity in (a), (b) and (c) can be explained as the result of equilibrium changes due to adsorption of ions such as $Al(OH)^{++}$ or AlO^+. Thus in a reaction of the following type:

$$Al^{+++} + H_2O \rightarrow Al(OH)^{++} + H^+$$
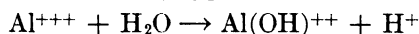
acidity would be expected to increase due to the removal of $Al(OH)^{++}$ or similar ions by adsorption. This view is strengthened by the results of the analysis of intermicellular liquid for aluminum, which together with the knowledge that essentially no chloride ion adsorption has taken place (except for freshly prepared hydrous alumina), establishes a ratio of equivalents of chlorine to aluminum of 1.04 to 1.00. Since the starting ratio of equivalents chlorine to alumina was 1.0 to 1.1 (for stock solution A) it appears probable that aluminum was adsorbed as a basic ion.

Furthermore, the adsorption of $Al(OH)^{++}$ and related ions, rather than Al^{+++} ions only, is in harmony with the principle of Gouy.[1] He believed that in the neighborhood of a charged plate the concentration of ions of like charge diminished exponentially as the valence increased. If this were true, ions having a positive valence of less than three would be expected to be present in the neighborhood of the positively charged particle in greater amount in proportion to the tervalent aluminum ion than in the bulk of the solution, and this would favor the adsorption of hydrogen ions and hydroxylated aluminum ions. But this adsorption may also be preferential in character, since if it depended only on charge, adsorption of such ions as $AlCl^{++}$ and $AlCl_2^+$ might be expected.

This adsorption does not explain the decrease of acidity upon settling, however, as shown in Table IV. It seems improbable also, in the case of coagulation (especially with sodium sulfate) that the observed results are due entirely to the displacement of adsorbed ions by the oppositely charged precipitating ion, so that they are again brought out into the solution, with corresponding effect on hydrogen ion concentration. A better explanation offers itself regarding these effects, which may well be a factor in all of the acidity changes observed. Gouy[1] has concluded that in the neighborhood of a charged plate there will be an excess of ions of opposite charge to the plate and a corresponding scarcity of ions of the same charge. Applying this to a colloidal solution containing many positively charged particles, one would expect the hydrogen ions not adsorbed by the particles to be present in lower concentration in the immediate vicinity of the particles than in the bulk of the solution.

Thus if the hydrogen electrode be considered to be positively charged, the hydrogen ion activity which it measured would consist of the activity in that part of the solution farthest removed from the particles, on account of the likeness of charge on the electrode and particles. Due to the repulsive effect of the particles on all positive ions, this activity would be expected to be slightly higher than if the particles were not present, since in the latter case, the space in the immediate neighborhood of the particles, which was sparsely occupied with hydrogen ions, would now become available to the crowded ions in the bulk of the solution. Any factor causing removal of particles, then, would be expected to cause a decrease of acidity in the bulk of the solution.

Two such factors are present, in precipitation and settling. In the former, the particles are removed from the system, and their charge is greatly diminished or even changed. In the latter, part of the particles are taken away from the system by gravity, and while their charge is probably not changed, its repulsive force is probably in part lost against the sides and bottom of the container. This inhibition of repulsive effect is thought to be one of the factors influential in causing the decrease of hydrogen ion activity observed during precipitation and settling.

[1] Gouy: J. Phys., (4) 9, 457 (1910).

A third source of increased activity of hydrogen ions is that due to the volume occupied by the colloidal particles. The aluminum chloride solutions were diluted in the one case by water, and in the other case by water plus colloid, so that the volume of the water actually added was slightly less. This factor must be very small, however, except in the case of the more concentrated sols.

The chloride ion activity measurements seem to have established the fact that essentially no chloride ion adsorption took place on the particles, except in the case of the two sols made from the hydrous alumina prepared only a few weeks.

The change in conductivity can be explained on the basis of adsorption. Thus the curve obtained in the conductance of basic aluminum chloride solution containing increasing amounts of colloidal alumina, as shown in Graph II, may be considered as the resultant of two curves, one sloping upward, corresponding to the increasing conductance of the colloid, as more and more of it was added; the other sloping down, corresponding to the decreasing conductance of the electrolyte as more and more of it was adsorbed on the particles. The decreasing volume of intermicellular solution between electrodes, due to the increasing volume of the colloid, would also be expected to cause a decreasing conductance.

In the method described here for the preparation of colloidal aged hydrous alumina, two factors enter into the treatment which evidently influence the purity of the resulting sols, and which have not usually been considered in previous methods of preparation of hydrous oxide sols. One is the allowance of plenty of time for aging (several weeks or months), and the other is the precaution of keeping excess ammonia present until all of the anion of the original salt has been removed. The aging is thought not to be necessary in the anion removal, since with a sample of hydrous oxide freshly precipitated from an aluminum chloride solution it was found possible to remove all of the chloride ion by repeated centrifuging in a few hours when a slight excess of ammonia was kept present. In the experiment just described, after all of the original anion had been removed, the sample was further centrifuged without addition of ammonia until the tendency to peptize began to overcome the centrifugal force. At this point considerable ammonia could still be detected with Nessler's reagent. At a corresponding point with the aged sols, on the other hand, the ammonia content was very much lower. Keeping the solution alkaline with ammonia is thought to be the condition necessary for complete removal of the anion of the original salt.

Summary

(1). A simple method has been described for the preparation of colloidal aged hydrous alumina.

(2) Using this method, colloidal aged hydrous alumina has been prepared from the nitrate, chloride and sulfate of alumina in which all of the anion of the original salt has been removed.

(3) The conclusion of Bradfield[1] that sulfate precipitation is reversible has been confirmed.

(4) The alumina prepared in this way contained ammonia in amounts as low as 1 equivalent to 25,000 equivalents of alumina, and a sol containing 0.05 equivalents of (colloidal) aged hydrous alumina per liter had a specific conductance as low as 6.6×10^{-6} mhos.

(5) The colloid was further stabilized by addition of basic aluminum chloride or hydrochloric acid.

(6) Equilibrium was established in a few days, using basic aluminum chloride. Many months were necessary for equilibrium to be established using hydrochloric acid.

(7) A study of ion distribution on sols stabilized with basic aluminum chloride has been made by means of hydrogen ion activity measurements, chloride ion activity measurements and conductance measurements. The results may be explained as being due to (a) adsorption of hydroxylated aluminum ions by the colloidal particles; (b) ion distribution in accordance with Gouy's conception of a diffuse outer double layer; (c) effect of the colloid on decreasing the volume of solution in a given amount of sol.

(8) The effect of the conditions of aging and alkalinity in the preparation of sols has been discussed.

(9) An unsuccessful attempt has been made to prepare two sols having just the same properties starting with aged hydrous alumina from two different aluminum salts.

[1] J. Am. Chem. Soc., **44**, 965 (1922).

INVESTIGATION OF THE DIFFERENTLY COLORED FORMS OF CERTAIN DERIVATIVES OF DIPHENYLAMINE

BY NICHOLAS MICHAEL CULLINANE, OLGA EDWINA EMBREY,
AND DANIEL RICHARD DAVIES

A considerable number of substances are described in the chemical litera-ture as existing in modifications of different color. In many cases the only differences in properties noted were the colors, in which the variations were usually not very pronounced. Such color differences can frequently be ac-counted for by the presence of traces of impurity, differences in the degree of fineness of the particles, differences in texture, and pleochroism, the forms being otherwise identical. Thus red phosphorus when fine-grained is scarlet in color, and when coarse-grained is violet. Further, the red and yellow forms of mercuric oxide are identical except in color. Mercuric iodide exists in two dimorphic forms, the red being stable below, and the yellow above, $128°$. Yet in liquid air the red form becomes yellow, and in liquid hydrogen, white.

The existence of a body in varieties of different color may also be due to polymorphism, and here differences in other physical properties besides color are observed, such as crystalline structure, melting point, solubility, density, these differences being found only in the solid state. On transformation of the solids into the liquid or the vapor state, or by solution, all differences be-tween the forms disappear.

Further, the alteration in color of a substance may be caused by change in chemical structure, for instance polymerisation, tautomerism, or stereoisomer-ism, and in cases of this type differences in properties will persist in the liquid state, or in solution, at least for some time.

Many organic compounds exist in forms of different color, but only in comparatively few cases have the crystallographical structures of physico-chemical properties been compared. In the present research a number of compounds were prepared in forms of varying color, and their crystalline structures, densities, solubilities, colors in different solvents and refractive indices of their solutions compared. In some cases the forms were found to be identical in all respects except color, some were shown to be dimorphic, and some were observed to exhibit chemical isomerism.

A. Hantzsch[1] has prepared several compounds which exist in modifications of different color, termed 'chromoisomerides,' and he attributes the change in color to change of structure. Among them are a number of nitroanilines, in-cluding some diphenylamines. The forms appear to differ only in the solid state, yielding with the same solvents optically identical solutions, possessing the same colors, refractive indices, and absorption spectra. He states that polymorphism is out of the question since solutions of certain 'chromoisomer-

[1] A. Hantzsch: Ber., **43**, 1662 (1910).

ides' in different media are different in color, and as the solute is found to be unimolecular it is assumed that the variation in color of the solutions is due to the presence of different 'chromoisomerides.'   However, it is shown in the present communication that similar variations in color in different solvents exist where there is no indication of chemical isomerism or even polymorphism. Such color differences may be due, at any rate in some cases, to the presence of solvates, for many such additive compounds, derived from diphenylamines, are known.   In fact Hantzsch,[1] in a later paper on acridine derivatives, postulates the formation of solvates to account for similar color variations.

Since 'chromoisomerism' as observed by Hantzsch appears to be evident only in the solid condition, in order to prove the existence of chemical isomerism he has recourse to a comparison of the physical properties of certain homologous series; for example, the members of the homologous series.

$$O_2N-\underset{}{\underset{}{\bigcirc}}-NR_2$$
with NO$_2$ substituent
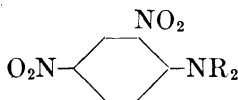
where R is methyl, ethyl or propyl, all give yellow solutions in chloroform, and the increments in molecular refraction on replacing methyl by ethyl, or ethyl by propyl, are respectively 9.5 and 9.4, these values being in close agreement with the theoretical value 9.2 (Brühl).   On the other hand, in the case of the corresponding 3:4-dinitroanilines, the solutions in pyridine of the dimethyl and diethyl derivatives are respectively yellow and orange, and the observed increment is 7.8 as compared with the theoretical value 9.2.   From this result Hantzsch concludes that the two substances cannot belong to an homologous series, but to two different isomeric series, and hence the difference in color is due to isomerism.   It seems quite likely, however, that this anomalous result is due to the formation in solution of different amounts of the additive compound of solvent and solute, for pyridine is basic and the nitroanilines slightly acidic.

Although in some cases the 'chromoisomeric' modifications of Hantzsch may be chemical isomerides, yet the existence of isomerism among the nitroanilines does not seem to have been satisfactorily proved by him.   His conclusions appear to be rather too far-reaching, for polymorphism is in most cases sufficient to account for his experimental results, and it is usual to assume the existence of polymorphism until there is satisfactory evidence of chemical isomerism.   It is also possible that in some instances the forms are actually identical save in color, for although sometimes the melting points differed, in many cases the only distinction observed was in color.

In the present research a number of nitrodiphenylamines of similar constitutions to those prepared by Hantzsch were examined.

2:4:6-Trinitro-4'-methyldiphenylamine (picryl-p-toluidine) exists in two forms, and a crystallographical investigation of them by Lenk[2] showed that

[1] Hantzsch: Ber., **44**, 1783 (1911).
[2] J. prakt. Chem., (2) **79**, 548 (1909).

the one modification was composed of yellow or orange-yellow monoclinic needles, and the other of dark red needles belonging to the rhombic system. The results obtained in the present research for the densities of the two forms confirmed this distinction but did not indicate whether the case was one of dimorphism or of chemical isomerism. However, it was further observed, contrary to the statement of Hantzsch[1] that solutions of picryl-p-toluidine in all media were orange in color, that the colors in solution varied considerably with the solvent, and furthermore that the colors of the two modifications in the same solvent differed considerably in some cases. Thus solutions of equal concentration in acetone were orange-red (yellow form) and orange with a yellow tint (red form); in pyridine very deep orange-red (yellow form) and reddish-orange (red form). In other media differences in color, though not so pronounced as in these two solvents, were also noticed. The yellow variety always gave the deeper color in solution. Molecular weight determinations in benzene proved here (as in the case of all the compounds examined) that both modifications were unimolecular. The refractive indices of solutions of equal concentration of the two forms in pyridine were different.

It was observed that the red form of picryl-p-toluidine yielded with benzene an orange-red solvate of different composition from that furnished by the orange-yellow variety. On heating, both additive compounds were converted into the red solvate-free form, while at the ordinary temperature both solvates were slowly transformed into the orange-yellow modification of the amine. Further, the latter form was changed into the red variety on heating alone or on standing in contact with acetone.
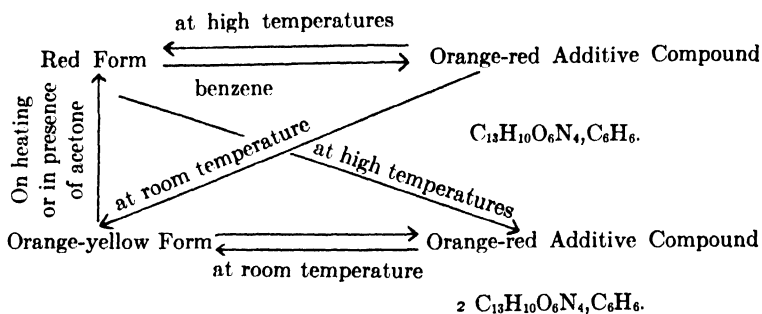
From the above results the two modifications of picryl-p-toluidine must be chemical isomerides.

It is interesting to compare the foregoing phenomena with those observed by P. Pfeiffer[2] and his coworkers in the case of certain nitro derivatives of stilbene. They found, for example, that 2-nitro-4'-methoxystilbene-4-carboxylic acid existed in a yellow and an orange form of identical melting point; these would normally be considered dimorphic modifications except that the following reversible phenomena occurred: the yellow acid gave an

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[1] Hantzsch: Ber., **43**, 1679 (1910).
[2] Ber., **48**, 1777 (1915); **49**, 2426 (1916); **51**, 554 (1918).

orange pyridine salt, whilst the orange acid gave a yellow pyridine salt of the same composition as the other, the acids being regenerated by treatment with hydrochloric acid. It was found possible to carry out the following reactions:

$$\begin{array}{ccc}
& \text{pyridine} & \\
\text{Orange Pyridine Salt} & \xrightarrow{} & \text{Yellow Pyridine salt} \\
\text{HCl} \downarrow \quad \uparrow \text{pyridine} & \text{heat} & \text{HCl} \downarrow \quad \uparrow \text{pyridine} \\
\text{Yellow Acid} & \xleftarrow{} & \text{Orange Acid}
\end{array}$$
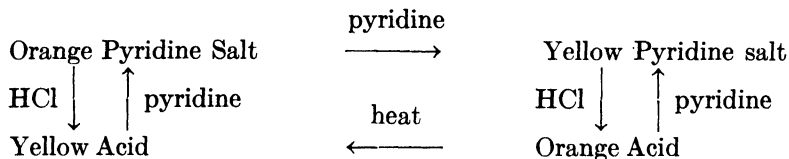
The different varieties of the one substance isolated by Pfeiffer yielded identical colors in a given solvent, but the colors varied considerably with the medium employed, this result being attributed by him to the formation in solution of different solvates, some of which were isolated.

The melting points of the two modifications of picryl-p-toluidine were observed to be the same, viz., 165.5°; this was evidently due to the conversion of one form into the other by heat, since the orange-yellow crystals on being heated gradually turned red at 150-155°. A mixture of the two varieties also gave the same melting point.

2:4-Dinitro-5-methyl-2'-methoxydiphenylamine was found by the present authors to occur in two forms of different color. These were then subjected to an optical and crystallographical examination. Owing to the specialised methods of preparation of the forms of this and the other substances herein described it was difficult in some cases to isolate suitable crystals, but in general the results confirmed those obtained by the physico-chemical methods. All the crystallo-optical examinations were carried out by Mr. A. Stuart. In the case of 2:4-dinitro-5-methyl-2'-methoxydiphenylamine he reports as follows:[1] "These two substances are crystallographically and optically distinct, the one being composed of brownish-yellow transparent monoclinic plates (which become yellow on being powdered) with a maximum extinction angle of 27°, and pronounced pleochroism, and the other of scarlet monoclinic needles with a maximum extinction angle of 5°, and pleochroism hardly noticeable. Different crystallographical forms occur in each and no angular measurements correspond."

The densities of the two substances were found to be different, and also the solubilities in chloroform. In contact with acetone the metastable form was transformed into the stable one (this occurred in the case of all the compounds investigated) and hence the solubilities in this solvent were observed to be identical within the limits of experimental error. No change of either modification took place in presence of chloroform. The stable variety was found to be less soluble than the metastable form.

The colors of solutions of 2:4-dinitro-5-methyl-2'-methoxydiphenylamine varied with the solvent employed; thus in benzene the color was orange, in acetic acid deeper orange, in alcohol and acetone a little deeper than in acetic acid, in chloroform reddish-orange, and in pyridine reddish-orange (slightly

[1] A more detailed and complete report will appear in a future communication.

deeper than in chloroform). The brownish-yellow modification gave a slightly deeper color in the last two media (in all experiments 0.1 g. of solute was dissolved in 30 g. of solvent). Also the refractive indices of solutions of equal concentration of the two forms in pyridine were quite different. Hence, the two modifications of 2:4-dinitro-5-methyl-2'-methoxydiphenylamine must be chemical isomerides.

The red form turned yellowish on heating, and accordingly the melting points of both varieties were the same.

2:4-Dinitro-5-methyl-4'-ethoxydiphenylamine also crystallised in two forms. Stuart reports: "The two substances are different in respect of color, crystal habit, transparency, and internal structure, one occurring in perfectly translucent bright-yellow monoclinic needles having an extinction angle of 31°; the other in rather opaque orange-red rhomb-like crystals giving no definite extinction between crossed nicols. The nature of these crystals precluded further investigation." The orange-red solid was produced by the action of heat on the yellow crystals. The latter when rapidly heated shrank considerably at about 125°, turning reddish, and then melted at the same temperature as the other modification. The transition point of the yellow variety is therefore in the neighbourhood of 125°.

The densities and solubilities in chloroform of the two forms were different. The bright-yellow modification is the stable one, and it was found to be less soluble than the orange-red solid. Solutions of equal concentration in the one solvent were identical in color, although the colors varied with the medium. The refractive indices of solutions of equal concentration in pyridine were identical within the limits of experimental error. As no differences in properties were observed except in the solid state the two forms of 2:4-dinitro-5-methyl-4'-ethoxydiphenylamine must be considered dimorphic.

2:4-Dinitro-2'-methoxydiphenylamine occurs in two forms of distinctive color, long thin orange-yellow needles and bright red needles. Stuart reports: "The two modifications are very much alike optically despite the startling difference in color. Both show that the length of the needles is the direction of fast vibration; pleochroism in each case is very slight, and extinction straight." The identity of the two modifications was proved by determinations of their densities and solubilities.

The orange-yellow variety on being heated became reddish at about 145° and melted at 165.5°, which was also the melting point of the red form. In a recent paper by Gallas and Alonso[1] a red modification of this compound is described, melting at 165°, and a yellow form which changed to red at 125-145° and melted at 153-159°. The two forms obtained by the present authors, however, tho prepared by the same methods as those employed by Gallas and Alonso, both melted at 165.5°.

The refractive indices of solutions of equal concentration of the forms were also approximately the same and both were observed to be unimolecular in benzene.

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[1] Gallas and Alonso: Anales Soc. Españ. Fís. Quím., **28**, 645 (1930).

	Benzene	Acetic acid	Acetone	Alcohol	Chloroform	Pyridine
2:4-Dinitro-5-methyl-4'-ethoxydiphenylamine. (both forms)	Orange.	Orange (slightly deeper than in benzene).	Orange (slightly deeper than in acetic acid).	Slightly deeper than in acetone.	Reddish-orange (slightly deeper than in pyridine).	Reddish-orange.
2:4-Dinitro -2'-methoxydiphenylamine. (both forms)	Orange.	Orange with red tint.	Orange with red tint.	Reddish-orange.	Reddish-orange (slightly deeper than in alcohol).	Deep reddish-orange.
Picryl Aniline. (both forms)	Orange-yellow.	Orange-yellow (slightly deeper than in benzene).	Deep orange-red.	Orange.	Orange with red tint.	Deep wine-red.
2:4-Dinitro -3'-methoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Slightly deeper than in acetone.	Orange (very slightly deeper than in pyridine).	Orange.
2:4-Dinitro-5-methyl-3'-methoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Very slightly deeper than in acetone.	Orange.	Orange (slightly deeper than in chloroform).
2:4-Dinitro-2'-ethoxydiphenylamine.	Yellowish-orange.	Orange (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Orange (slightly deeper than in acetone).	Reddish-orange (slightly deeper than in pyridine).	Reddish-orange.
2:4-Dinitro-3'-ethoxydiphenylamine.	Yellow.	Slightly deeper than in alcohol.	Yellow with orange tint.	Orange-yellow (slightly deeper than in acetone).	Very slightly deeper than in pyridine.	Orange.
2:4-Dinitro -5-methyl-2'-ethoxydiphenylamine.	Orange-yellow.	Orange (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Very slightly deeper than in acetone.	Reddish-orange.	Reddish-orange (slightly deeper than in chloroform)
2:4-Dinitro-5-methyl-3'-ethoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in acetone).	Very slightly deeper than in alcohol.	Slightly deeper than in benzene.	Orange.	Orange (slightly deeper than in chloroform).

In the case of this substance the physical properties (except the colors) of the two modifications were the same and the colors of solutions of equal strengths in the one solvent were identical, yet the color varied considerably with the medium employed altho there was no indication of isomerism or even polymorphism.

2:4:6-Trinitrodiphenylamine (picryl aniline) was isolated as large reddish-orange monoclinic prisms with a mauve colored reflex and also as very small bright-yellow prisms which were similar in appearance, but a complete examination was not possible owing to their minute size. Both varieties melted at 180.5°. It was noticed that the larger crystals varied from red to orange in color, the exact hue appearing to depend upon their size (in all cases yellowish crystals were formed on powdering). This possibly accounts for the various descriptions of the amine in the literature, deep red prisms,[1] scarlet prisms,[2] orange needles,[3] yellow needles.[4] Bamberger and Müller[5] considered that there were two forms, orange-red needles and scarlet-red prisms, while Hantzsch[6] stated that there was only one, a reddish-orange, modification.

The two varieties prepared by us gave the same density, and the solubilities in acetic acid and in chloroform were likewise identical. The colors of the two modifications in the same solvent were alike, but they varied considerably in different media. The forms were both found to be unimolecular in benzene, and the refractive indices of solutions of equal concentration in pyridine were in close agreement.

The only difference then noted between the two varieties of picryl aniline was the color; they were identical in all other properties examined.

Table I gives a comparison of the colors of solutions of the compounds in various solvents, and also of some other substances (obtained in one form only) of analogous constitutions. The colors were compared by means of a Klett Top Reader Colorimeter (in all cases 0.1 g. of solute in 30 g. of solvent was taken).

Experimental Part

Before carrying out the experiments described below each compound was first of all completely purified by repeated recrystallisation. Then the two forms were prepared and examined.

The density determinations were carried out by means of a 25 cc. Regnault density bottle, the specific gravities of both solids being determined simultaneously under identical conditions. Water was found to be an unsuitable liquid to use for in most cases the solids floated (partly at least) on the surface, and also it was not easy to remove air bubbles completely. Light petroleum ether (b.p. 40°-50°), the density of which is considerably lower than that of

[1] Ullmann and Nadai: Ber., 41, 1876 (1908).
[2] Sudborough and Picton: J. Chem. Soc., 89, 583 (1906).
[3] Leemann and Grandmougin: Ber., 41, 130 (1908).
[4] Giua and Cherchi: Gazz., 49 II, 152 (1919).
[5] Ber., 33, 108 (1900).
[6] Hantzsch: Ber., 43, 1678 (1910).

water, was found to be quite satisfactory. Only a minute trace of either modification dissolved in this liquid, nevertheless a solution of the light petroleum ether saturated at the temperature of the experiment with the substance was employed. Any slight differences in solubility between the forms was negligible. Air bubbles were removed by connecting the pyknometer to the pump. The bottle was placed in a vessel of water at the required temperature for a half hour before each weighing was taken.

For the determination of the solubilities excess of each solid together with the purified solvent was placed in a flask, fitted with a ground-glass stopper, and immersed in a thermostat at the required temperature, which did not vary by more than 0.1°. The mixture was frequently shaken until equilibrium was attained. A portion of the solution was then transferred to a weighing bottle by means of a pipette (also at the thermostat temperature). The latter consisted of a glass tube closed at one end and containing near the closed end a small hole corresponding to which was a similar hole in the ground-glass neck of the bottle. By rotation of the stopper in the neck the two holes could be brought into coincidence, and by this means the pressure inside the vessel was made equal to the atmospheric pressure, and then by further rotation of the stopper the bottle was made airtight. The weighing-bottle and contents were then weighed and the solvent evaporated off to constant weight.

The refractive indices of solutions of each form were determined for sodium light in pyridine by means of a Pulfrich refractometer; and the molecular weights were determined cryoscopically.

The solvents used were purified as follows. Benzene was obtained pure by removal of thiophene by means of concentrated sulphuric acid, drying over calcium chloride, and distilling. Then it was thrice frozen, dried again, distilled from sodium and fractionated. The acetone after standing over potassium permanganate was distilled, converted into the sodium iodide derivative, and again distilled. After standing over calcium chloride it was once more distilled, treated with potassium carbonate and fractionated. The chloroform was successively washed with sodium hydroxide, hydrochloric acid, and water, dried by means of calcium chloride, and distilled from phosphoric oxide. The pyridine was refluxed with quicklime and fractionally distilled. The acetic acid was partially frozen thrice, fractionally distilled, dried, and again fractionated.

2:4:6-Trinitro-4'Methyldiphenylamine (*Picryl-p-Toluidine*). The orange-yellow form of this compound, according to Busch and Pungs,[1] was got by addition of hydrogen chloride to a solution of the amine in alcohol containing some alkali, and according to Hantzsch[2] by recrystallization from chloroform, carbon tetrachloride, benzene or acetone. It was found by the present authors that by evaporation at the ordinary temperature of a solution of moderate concentration in acetone the orange-yellow crystals were usually produced. It was, however, difficult in most cases to prepare the orange-yellow variety uncontaminated by the red. From a solution in alcohol containing a little

[1] Busch and Pungs: J. prakt. Chem., (2) **79**, 547 (1909).
[2] Hantzsch: Ber., **43**, 1679 (1910).

hydrochloric acid the orange-yellow solid first separated, but this partly changed on standing to the red form. From benzene an orange-red solvate resulted. The orange-yellow modification was best obtained by recrystallization of the mixed forms or even of the red form from hot carbon tetrachloride. The statement of Busch and Pungs that the red variety can only be converted into the orange-yellow form thro the alkali salt is therefore incorrect.

The red form is the stable one and separates from hot concentrated solution in acetone. It is readily obtained pure for the orange-yellow modification on standing in presence of acetone is transformed in a short time into the red compound. According to Busch and Pungs it can also be obtained from benzene containing some alcohol and also from alcohol to which ammonium hydroxide has been added. This form is also said to be deposited from dilute solution in alcohol, and from pyridine.

The melting point of the red modification is given by Busch and Pungs as 165°, two degrees higher than that of the orange-yellow form. Hantzsch states that both substances melt at 164°, while Ullmann and Nadai[1] describe picryl-p-toluidine as red needles melting at 169°. It was observed in the present work that the melting points of both forms were the same, viz. 165.5°, the orange-yellow crystals on being heated turning red gradually. It was remarked that after heating the orange-yellow variety above its melting point yellow and red crystals separated out side by side on cooling. Prolonged . heating of the orange-yellow solid to a temperature just below its melting point caused it to be completely converted into the red.

Two additive compounds with benzene were isolated. The orange-yellow crystals were dissolved in boiling benzene and on allowing the solution to cool orange-red needles separated out. These were dried rapidly and a weighed portion heated to 100° for several hours until the weight was constant.

Wt. of sample G.	Benzene found %	Benzene calcd. for $2C_{13}H_{10}O_6N_4, C_6H_6$
1.5939	11.0	10.9

On heating this solvate it shrank slightly at about 100-110° and reddened somewhat, becoming quite red at 155-160° and melting at 165.5°. After several weeks at the ordinary temperature it changed into the orange-yellow form of picryl-p-toluidine.

Similar experiments were carried out with the red modification of the amine. The solvate, obtained in the same way as that from the orange-yellow variety, gave the following results on analysis:

Wt. of sample G.	Benzene found %	Benzene calcd. for $C_{13}H_{10}O_6N_4, C_6H_6$
0.6605	20.4	19.7

This solvate also shrank on heating at about 100° and deepened in color. At about 150° it became quite red and melted at 165.5° to a deep-red liquid.

[1] Ullmann and Nadai: Ber., **41**, 1876 (1908).

The densities of the two forms of picryl-p-toluidine were determined by the method above described and gave the following results:

	Temp. o	Density g./ml.
Orange-yellow form	14.2	1.467
Deep-red form	14.2	1.626

The molecular weights of the two forms were determined cryoscopically in benzene, the freezing constant for the solvent being found by a separate experiment.

	Mol. wt. found	Mol. wt. calcd. for $C_{13}H_{10}O_6N_4$
Orange-yellow form	314; 323	318
Deep-red form	318; 315	318

The refractive indices of solutions of the two forms gave the following results:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Orange-yellow form	Pyridine	5	Absorption too great; no reading	——
Deep-red form	Pyridine	5	34°38.5′	1.51785
Orange-yellow form	Pyridine	2.5	35°33.5′	1.51289
Deep-red form	Pyridine	2.5	35°44.5′	1.51189

2:4-Dinitro-5-Methyl-2'-Methoxydiphenylamine. This compound was obtained in two modifications. As a rule slow crystallization at the ordinary temperature from acetone yielded large brownish-yellow transparent crystals melting at 146° to a deep-red liquid. Slow evaporation of the solvent from a solution in light petroleum ether at the ordinary temperature, or separation from hot alcohol gave in most cases this form also, which was the stable one, for on allowing the other variety to stand in presence of acetone in the cold it reverted in a short time to the yellow modification.

By crystallization from a hot solution in acetone the brownish-yellow crystals were found to be mixed with red needles, which could be obtained in small quantity free from the other form by mechanical separation. On adding cold light petroleum ether to a warm moderately concentrated solution in benzene red mixed with yellow crystals were deposited. The red solid became yellowish on heating; its melting point was also 146° and was undepressed by admixture with the other modification. The preparation of the red variety in quantity uncontaminated by the yellow was difficult. The most satisfactory method consisted in refluxing the amine for 30 mins. with a large volume of light petroleum ether (60-80°) containing a little benzene, then decanting rapidly thro a hot filter into an ice-cooled flask. The latter was continuously shaken and the red solid filtered off and dried.

2:4-Dinitro-5-methyl-2'-methoxydiphenylamine was found to be readily soluble in benzene, acetone, chloroform, or pyridine, moderately soluble in alcohol, and sparingly soluble in light petroleum ether.

Anal. Calcd. for $C_{14}H_{13}O_5N_3$: C 55.4, H 4.7, N, 13.9. Found (brownish-yellow form) C 55.1, H 4.5, N, 13.9; (red form) C 55.2, H 4.4, N 13.9.

The following results were obtained for the densities of the two forms:

	Temp. o	Density g./ml.
Red form	15.2	1.485
Brownish-yellow form	15.2	1.414

Red form after standing in contact with acetone for three days, the color having changed to yellow:

	15.2	1.411

The last result shows that the red modification was converted into the yellow in presence of acetone. Hence, the solubilities of both varieties were found to be the same in this solvent. In chloroform no change in color occurred and the solubilities of the two forms in this medium were quite different.

	Temp. o	Solvent	Solubility G. solute in 100 g. soln.
Brownish-yellow form	24.5	Acetone	4.685
Red form	24.5	Acetone	4.691
Brownish-yellow form	31.93	Acetone	5.853
Red form	31.93	Acetone	5.853
Brownish-yellow form	31.95	Chloroform	15.861
Red form	31.95	Chloroform	16.998

The molecular weights determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{14}H_{13}O_5N_3$
Brownish-yellow form	305	303
Red form	307	303

The refractive indices of solutions of both forms at 20° were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Brownish-yellow form	Pyridine	5	34°49'	1.51691
Red form	Pyridine	5	35°3'	1.51565

2:4-Dinitro-5-Methyl-4'-Ethoxydiphenylamine. The original product was dark in color, but a more light-colored compound was obtained by dissolving the substance in acetic acid and pouring the solution into much water with vigorous shaking. It was then washed with water and recrystallized several times.

From hot acetone-alcohol by rapid cooling bright-yellow crystals were obtained melting at 148.5°. Similarly rapid recrystallization from warm solutions in either of these solvents or precipitation from cold moderately concentrated solution in benzene by means of light petroleum ether yielded the yellow form, which was the stable one.

A second modification was formed by heating the yellow solid to 130° for several hours, the product consisting of orange-red crystals.

Both varieties were readily soluble in hot acetone, benzene, acetic acid, pyridine, or chloroform, slightly soluble in alcohol, and sparingly soluble in light petroleum ether.

As the yellow form was converted into the orange-red on heating without loss in weight the former only was analysed.

Anal. Calcd. for $C_{15}N_{15}O_5N_3$: N, 13.25. Found: N, 13.4.

The densities of the two modifications were different, but after standing in presence of acetone the density of the orange-red crystals was observed to be approximately the same as that of the yellow, the specific gravity of which was unaffected by similar treatment.

	Temp. °	Density g./ml.
Bright-yellow form	14.2	1.444
Orange-red form	14.2	1.371

Orange-red form after standing in presence of acetone for 3 days, the color having changed to yellow:

	14.2	1.445

As the orange-red form was transformed into the yellow in acetone the solubilities of both were in close agreement in this solvent. In chloroform no color change of either form was noted and their solubilities were different in this medium.

	Temp. °	Solvent	Solubility G. solute in 100 g. soln.
Bright-yellow form	31.8	Acetone	7.756
Orange-red form	31.8	Acetone	7.757
Bright-yellow form	37.1	Acetone	9.789
Orange-red form	37.1	Acetone	9.792
Bright-yellow form	31.95	Chloroform	19.104
Orange-red form	31.95	Chloroform	19.343

The following results were obtained for the molecular weights, determined cryoscopically in benzene:

	Mol. wt. found	Mol. wt. calcd. for $C_{15}H_{15}O_5N_3$
Bright-yellow form	313	317
Orange-red form	315	317

The refractive indices of solutions of the two modifications were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Bright-yellow form	Pyridine	5	$35°27'$	1.51358
Orange-red form	Pyridine	5	$35°25'$	1.51366

2:4-Dinitro-2'-Methoxydiphenylamine. The condensation product was purified by repeated recrystallization from acetone. The two forms were prepared by the following methods, which, however, could not always be repeated:

By allowing a hot concentrated solution in alcohol to cool slowly the scarlet variety separated out.

On rapid cooling of a warm solution of moderate concentration in acetone orange-yellow flocculent crystals were deposited. This modification was also formed by slow evaporation from a solution in alcohol-acetone. Recrystallization from hot alcohol yielded at a high temperature the red solid; when the solution had cooled to just above the room temperature the orange-yellow crystals were produced.

2:4-Dinitro-2'-methoxydiphenylamine was found to be soluble in hot acetone, chloroform, pyridine, or glacial acetic acid, moderately soluble in alcohol, and sparingly soluble in light petroleum ether.

As the orange-yellow modification became red on heating without loss in weight the former only was analysed.

Anal. Calcd. for $C_{13}H_{11}O_5N_3$: N, 14.5. Found: N, 14.45.

The densities of the forms were as follows:

	Temp. o	Density g./ml.
Orange-yellow form	14.4	1.468
Scarlet form	14.4	1.464

The solubilities of both forms were in very close agreement.

	Temp. o	Solvent	Solubility G. solute in 100 g. soln.
Orange-yellow form	31.5	Acetone	4.467
Scarlet form	31.5	Acetone	4.461
Orange-yellow form	37.1	Acetone	5.461
Scarlet form	37.1	Acetone	5.467
Orange-yellow form	29.8	Chloroform	7.979
Scarlet form	29.8	Chloroform	7.960

The molecular weights, determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{13}H_{11}O_5N_3$
Orange-yellow form	271; 282	289
Scarlet form	281; 285	289

The refractive indices of solutions of the two forms were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Orange-yellow form	Pyridine	5	$34°45'$	1.51727
Scarlet form	Pyridine	5	$34°44'$	1.51736

2:4:6-Trinitrodiphenylamine (Picryl Aniline). By slow crystallization of the above compound from acetone at the ordinary temperature reddish-orange crystals separated. Crystals of the same color were also obtained from alcohol, even when some hydrochloric acid was present.

On pouring a fairly dilute solution of the diphenylamine in boiling acetic acid into a large volume of water with vigorous agitation small bright yellow crystals were precipitated. These were immediately filtered, washed with water, and dried.

The densities of the two varieties were as follows:

	Temp. o	Density g./ml.
Bright-yellow form	14.1	1.571
Red-orange form	14.1	1.570

The following results were obtained for the solubilities of the two forms:

	Temp. o	Solvent	Solubility G. solute in 100 g. soln.
Bright-yellow form	24.3	Acetone	7.665
Red-orange form	24.3	Acetone	7.658
Bright-yellow form	29.3	Acetone	8.551
Red-orange form	29.3	Acetone	8.567
Bright-yellow form	14.5	Acetic acid	0.7580
Red-orange form	14.5	Acetic acid	0.7555
Bright-yellow form	24.3	Acetic acid	0.9065
Red-orange form	24.3	Acetic acid	0.9036
Bright-yellow form	29.8	Chloroform	1.483
Red-orange form	29.8	Chloroform	1.489

The molecular weights determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{12}H_9O_6N_4$
Bright-yellow form	306	304
Red-orange form	311	304

The refractive indices of solutions of the forms were in close agreement.

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Bright-yellow form	Pyridine	5	$34°38'$	1.51790
Red-orange form	Pyridine	5	$34°39'$	1.51781

In conclusion we wish to express our thanks to Prof. W. J. Jones for his valuable suggestions, and also for his help in the determination of the refractive indices.

Summary

1.   2:4:6-Trinitro-4'-methyldiphenylamine exists in two modifications of different color, crystalline structure, and density. Moreover each form yields a different additive compound with benzene, and solutions of equal concentration in pyridine possess different colors and refractive indices. The two forms are therefore chemical isomerides.

2.   The two forms of 2:4-dinitro-5-methyl-2'-methoxydiphenylamine are different in color, crystallographical properties, density, and solubility. Solutions of equal strength in pyridine are different in color and refractive index. Hence, the two modifications are also isomeric forms.

3.   The two modifications of 2:4-dinitro-5-methyl-4'-ethoxydiphenylamine are dissimilar in crystallo-optical properties, density, and solubility. As no distinctions were observed except in the solid state they are considered to be dimorphic forms.

4.   The two forms of 2:4-dinitro-2'-methoxydiphenylamine and of 2:4:6-trinitrodiphenylamine are of distinctive color. The modifications appear to be similar in crystallographical properties, and their densities, solubilities, colors and refractive indices of solutions of equal concentration are in very close agreement. The two forms are therefore identical save in color.

University College,
Cardiff, Wales.
February 5, 1932.

THE DETERMINATION OF ALUMINUM AND OF EXCESS ACID IN ALUMINUM SALTS*

BY HERBERT L. DAVIS

Certain salts of aluminum, notably the sulphate and the chloride, have important industrial uses in water purification, textile mordants, paper sizing, etc. These salts, however, in common with certain other similar salts, do not crystallize ordinarily in the pure state, but, unless special precautions are taken, will be found to contain more or less than the theoretical amount of acid. The determination of the deviation of a given salt from the composition of the neutral salt has been made the object of numerous investigations and each author of a text or handbook on industrial analysis gives his favorite method. The present paper will describe a method which for speed and simplicity appears to be definitely superior to the methods in common use. This method is an extension of a previous paper[1] in which it was demonstrated that the amount of aluminum present in a salt known to be a normal salt free from excess (or deficiency) of acid could be determined by a simple titration with standard alkali in the presence of phenolphthalein if the system be boiled sufficiently to displace the acid adsorbed on the alumina. This titration is equally valid if thymol blue be the indicator used and this indicator permits the determination of the free acid since aluminum chloride and aluminum sulphate give solutions which lie within the intermediate yellow color range and a slight excess of acid depresses the pH value so as to show the red color.

In the paper referred to above a study was made of the titration curves of aluminum chloride and of aluminum sulphate with alkali, and a comparison was made with similar curves obtained by Hildebrand[2] and by Blum.[3] The curves of these authors showed initial portions in which on addition of alkali the pH of the solutions changed in about the manner shown by the last addition of alkali to a solution of hydrochloric acid. The fact that these initial portions were absent from our determinations and from other experiments in the literature on salts known to contain no excess acid pointed to their explanation as being due to excess acid. The present paper confirms this explanation and utilizes it for the measurement of the amount of free acid present.

The curves of Hildebrand and of Blum are neither self-consistent nor in accord with the facts but we may take as our starting point the data gathered recently by Miss Farnham. She reported that salts of aluminum known to be neutral showed the following pH values.

* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Davis and Farnham: J. Phys. Chem., 36, 1057 (1932).

[2] Hildebrand: J. Am. Chem. Soc., 35, 863 (1913).

[3] Blum: J. Am. Chem. Soc., 35, 1499 (1913).

TABLE I

The pH of Solutions of Aluminum Salts

	N	0.3 N	0.1 N
Aluminum chloride	2.3	2.9	3.0
Aluminum sulphate	2.8	3.0	3.4

These figures are in agreement with the well-known greater acidity of solutions of aluminum chloride than of solutions of the sulphate and the change with dilution is the expected one. On adding alkali to these solutions the pH changes rather slightly until about two thirds of the theoretical amount of alkali has been added. This buffer action is quite marked and has recently been used satisfactorily to buffer an oxidation-reduction reaction. In the case of the chloride such a system will be quite clear, the alumina being peptized by the aluminum and hydrogen ions remaining.

The curves of Hildebrand and of Blum indicate and our own experiments confirm that the addition of a small amount of excess acid depresses the pH value sharply. The excess acid could of course be determined from the pH titration curve electrometrically but this method is somewhat cumbersome and such a titration cold cannot be used to determine the amount of aluminum present. Both parts of the problem could be solved by the use of indicators changing color at the appropriate values which should be a little less than pH 3 for the excess acid and about pH 8 for the aluminum. Thymol Blue is almost ideal for such a titration since its colors and ranges are:

Red 1.2 — 2.8 Yellow 8.0 — 9.6 Blue

Tests show that it is entirely suitable if certain precautions be observed.

In the first place it was established that thymol blue gives results which are perfectly reliable in the titration of normal solutions of aluminum chloride or aluminum sulphate with 1.19 N NaOH. This titration is essentially the titration of the strong acids freed by hydrolysis and these acids are adsorbed strongly by the alumina unless the systems be boiled while slightly alkaline until no more alkali is neutralized and then the slight excess of alkali is titrated with standard acid. The change from the yellow to blue of thymol blue is not quite so easily perceived as is the change from colorless to red of phenolphthalein, but is perfectly satisfactory and accurate.

Then came the more important problem of the free acid. Consideration of an ordinary titration curve of a strong acid with alkali will show that an indicator changing over the range from 1.2 to 2.8 should not give a sharp color change but will require several drops of alkali to change from the full red to the full yellow and that it will require two or three drops more of alkali to produce a pH of 8 corresponding to the first appearance of the blue of thymol blue. This was all confirmed for thymol blue and in addition it was found that if one dissolved five grams of sodium chloride in fifteen cc of water, one drop of normal hydrochloric acid produces a very deep red color of the indicator. Without the salt the effect of the acid is plainly perceptible but blank solutions are a necessity for comparison while with the salt the color change produced is

much more marked. This increase in the chemical potential of the hydrogen ion by adding salt is found to be a very useful property in the present method, for it was found that accurate analysis of the aluminum sulphate required the addition of salt.

One of the first questions to be answered was one having to do with the effect of concentration of the aluminum salts. A sample of aluminum chloride was dissolved cold in a small amount of water and diluted in steps, four drops of thymol blue being added to each of four eight cc samples. It was then found that a solution 1.7 N with $AlCl_3$ was very faintly acid (showed a slight reddish tinge) while the solutions 0.85 N was fully yellow and was given a distinct red tinge by the addition of one drop of normal hydrochloric acid. This confirmed previous experience that normal $AlCl_3$ solutions were quite satisfactory in that the excess of acid added to them could be titrated sharply by adding alkali to the pH 2.8 point.

With aluminum sulphate, a solution 4.2 N gave a faint reddish tinge, while solutions 2.1 N or less were fully yellow. These more dilute solutions did not develop the red color even with two drops of normal acid until one gram of sodium chloride was added to each eight cc solution when all became distinctly reddish. In the absence of sodium chloride some buffer action still persists, probably an adsorption of acid on alumina produced by hydrolysis which is well known to be greater in the sulphate than in the chloride solutions. Two grams of sodium chloride added to ten cc of normal aluminum sulphate solution gives only a very faint reddish tinge since it activates the sulphuric acid produced by the hydrolysis, but the salt makes the indicator change much sharper when excess acid is added. The combined effect of high salt concentrations, excess acid, and heating results in the coagulation of some of the thymol blue and for this reason heating of such systems is not recommended, especially in the case of the sulphate solutions.

These preliminary experiments establish the method as reliable and this was borne out by numerous titrations. For the most part these started with normal solutions of aluminum chloride or sulphate and it is suggested that an unknown salt to be examined be dissolved in sufficient water to give about a normal solution. The acid and alkali used were 0.97 N and 1.24 N, respectively. The simplest method is to add a known excess of acid to a known solution of aluminum salt and then add alkali until the final disappearance of the red tinge of the indicator. In practice it was found that a better method is to add sufficient alkali to produce a definite yellow color, permit the alumina precipitated by the local high concentration of the alkali drops to redisperse and then to add acid to the clear yellow solution to the first appearance of the reddish tinge corresponding to pH 2.8. This will give a rapid measure of the free acid present which will ordinarily be accurate to less than two percent. It is then a simple matter to continue adding alkali and, with heating, titrate to find the alkali needed to precipitate the alumina or rather to neutralize the acid resulting from the hydrolysis of the normal aluminum salt. Two samples of our aluminum sulphate (from Baker) were neutral in being without excess acid and showed 15.6 and 15.7% alumina while gravimetric determinations

showed 15.7 and 15.8% alumina. With aluminum sulphate it is necessary to add about two grams of pure sodium chloride for each ten cc of titrating solution. This sharpens the color change at the neutralization of the excess acid and does not affect the final determination of the amount of aluminum present.

As has been pointed out, it is more difficult to see the last disappearance of the red tinge at pH 2.8 than its first appearance on adding acid and, furthermore, the precipitation of alumina obscures this end point when it is being reached by adding alkali to the system. In certain respects, therefore, it is desirable to follow another procedure. To the system containing aluminum salt and excess acid, a known amount of standard alkali is added until the alumina is redissolved and repeptized to a practically clear system colored deep blue by the thymol blue indicator. Then standard acid is added cold until the last blue tinge of the indicator changes to the full yellow at pH 8. This amount of acid is an accurate measure of the excess of alkali added. Then the addition of acid is continued until a drop gives the first appearance of the red tinge. This acid is an accurate measure of the aluminum present. Heating is permissible in the chloride solutions but not in the sulphate solutions and salt addition should be made to the latter. The difference between the equivalents of alkali originally added and the total amounts of acid used to titrate back to pH 2.8 is a measure of the excess acid present. If we represent the acid and alkali used in terms of cc of normal reagent, we have;

A = Total normal cc of alkali added to produce clear system.
B = Excess alkali added above that required to reach pH 8.
C = Alkali equivalent to the aluminum present.
D = Alkali equivalent to the excess acid present.

$$A = B + C + D \qquad \text{and} \quad A - (B + C) = D$$

In that thymol blue gives the dividing lines between B and C and between C and D, it is most admirably suited for the rapid and accurate solving of this problem.

This second procedure points at once to the solution of another problem in permitting the equally rapid analysis of so-called sodium aluminate solutions. Lunge and Keane[1] say of this compound: "Sodium aluminate is used in dyeing, printing, in preparing lakes, and sometimes in sizing paper: also in the manufacture of milk glass, for hardening bricks and in soap making. The analysis is generally limited to the estimation of sodium oxide and of alumina; impurities such as insoluble matter, silica, and iron are sometimes determined." They determine alumina by precipitating it with carbon dioxide until the color of phenolphthalein is discharged and in the filtrate from the alumina the sodium carbonate is titrated with standard acid and methyl orange. It is obviously much more simple and rapid to titrate the sodium aluminate with standard acid and thymol blue first to the discharge of the blue color to determine the alumina present and then to titrate to the appearance of the red tinge to determine the alumina present. Hydrochloric acid is greatly to be preferred over sulphuric for this titration.

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[1] Lunge and Keane: "Technical Methods of Chemical Analysis," 2, 375 (1928).

The general scheme of these titrations is to be found in the work of Bayer[1] who used the titrations with tropaeolin oo [red (1.4 − 2.6) yellow] and with litmus. The difference between these titrations represented aluminum. It is not clear that Bayer used the method directly for excess acid but that may be read into his paper which is quite complete. Schmatolla[2] titrated neutral aluminum sulphates with phenolphthalein and Kolthoff[3] and Tingle[4] have used the same procedure.

Other methods for the determination of excess acid include an extraction of the salt with alcohol to take out the acid.[5] Another general device is to remove the aluminum ion so that it cannot take part in the acid-base reaction. One method is to convert it into the insoluble $AlF_3.3KF$ by adding an excess of potassium fluoride[6] or to put the aluminum ion into the complex ion[7] of the salt $K_3Al(C_2O_4)_3$ and the excess acid can then be titrated. Feigl and Kraus determine the free acid after their treatment as did Stock[8] directly without such treatment.

Methyl orange has been used and its lower limit (2.9 to 3.1, depending on the product) would probably be suitable. The color change with thymol blue is easier to see and only the one indicator is needed. The use of methyl orange and phenolphthalein[9] for the zinc salts is relevant. The modern theory of pH and indicators is a helpful generalization for application in such titrations as these.

Summary

1. The earlier work on the volumetric determination of aluminum in solutions of its salts has been extended to include a similar method for the excess acid sometimes found in such solutions.

2. Using thymol blue as the indicator it has been shown to be possible to titrate first the excess acid and then the aluminum present in a sample of salt. If the salt is a basic salt then a portion of a known excess of standard acid will be used in correcting this and the remainder will be titrated by the method.

3. The determination of sodium oxide and of alumina present in a sodium aluminate solution can be made similarly by the use of the same indicator.

Cornell University.

[1] Bayer: Z. anal. Chem., **24**, 542 (1885).

[2] Schmatolla: Ber., **38**, 985 (1905).

[3] Kolthoff: Z. anorg. Chem., **112**, 185 (1920).

[4] Tingle: J. Ind. Eng. Chem., **13**, 420 (1921).

[5] Williams: Chem. News, **56**, 194 (1887); Beilstein and Grosset: Z. anal. Chem., **29**, 73 (1890); J. Soc. Chem. Ind., **9**, 416 (1890).

[6] Craig: J. Soc. Chem. Ind., **30**, 184 (1911).

[7] Feigl and Kraus: Ber., **58B**, 398 (1925).

[8] Stock: Compt. rend., **130**, 175 (1900); J. Soc. Chem. Ind., **19**, 276 (1900); J. Chem. Soc., **78**, 247, 315 (1900).

[9] Lescoeur: Bull., (3) **13**, 280 (1895).

THE MICROSCOPIC METHOD OF ELECTROPHORESIS

BY HAROLD A. ABRAMSON

In a recent discussion of the microscopic method of determining the mobilities of microscopically visible particles Mukherjee[1] has pointed out certain difficulties which, he believes, lessen the precision at present attainable in measurements of this sort. These criticisms certainly do apply in poorly conducted experiments, not only for the microscopic method but for all measurements of electric mobility including ionic mobilities. It may be of interest to investigators to know that with the technic devised by Northrop and Kunitz[2] and as employed by the writer[3] the experimental difficulties (quoted and italicized below) mentioned by Mukherjee are eliminated.

1. *"Firstly, there is an error in calculating the potential gradient."*

It has been shown that the electric field is uniform and that the field strength, X, can be accurately calculated within the limits of error by means of Ohm's law

$$X = IR/q$$

(I = current; R = specific resistance of the suspension; q = cross-section of the electrophoresis cell).[2,3]

2. *"Secondly, disturbances arising out of 'polarization' and electrolysis are greater in these small vessels."*

Non-polarizable electrodes are employed in a fashion which excludes contamination due to electrolysis.[2,3,4]

3. *"The third and most important consideration is that particles stick to the walls forming patches of surface of different properties."*

The cell can easily be cleaned with cleaning mixture or any solvent between measurements for it is made of one piece of glass, having no rubber connections. Further, since measurements of any one system need not take more than three minutes, asymmetry of the cell due to differences of the walls need under most circumstances not be greater than the limits of experimental error. The cell can also be used vertically with large oil droplets.

College of Physicians and Surgeons,
Department of Biological Chemistry,
630 West 168th Street,
New York City.

[1] J. N. Mukherjee: J. Phys. Chem., **36**, 595 (1932).

[2] J. H. Northrop and M. Kunitz: J. Gen. Physiol., **7**, 729 (1925).

[3] H. A. Abramson: J. Gen. Physiol., **12**, 469 (1929); H. A. Abramson and E. B. Grossman: **14**, 563 (1931).

[4] K. Ellis: Z. physik. Chem., **78**, 321 (1911).

THE PEPTIZATION OF CUPROUS OXIDE AND THE ELECTRO-DEPOSITION FROM AND DECOLORIZATION OF AMMONIACAL COPPER SOLUTIONS

BY E. A. VUILLEUMIER

When copper is plated from an ammoniacal cupric solution the deposit obtained is relatively dense, smooth and adherent. The author observed, however, some years ago, that when the electrolyte had been in contact with metallic copper for a few hours prior to the electrolysis there was a striking change in the nature of the deposit to be obtained. It then consisted of a dull red, thick, moss-like, coarse, non-adherent mass, which under a low power microscope was seen to consist of relatively large, bright copper crystals. It was also observed that upon the addition of concentrated ammonia or ammonium sulphate (but not sodium sulphate), or by thorough oxidation by aeration of the partially reduced electrolyte good results, i.e., dense, smooth, adherent deposits were again obtainable.

The present investigation indicates that a cuprous oxide cathode film is responsible for the unsatisfactory deposit; that an electrolyte from which an unsatisfactory deposit is obtained is one which does not peptize cuprous oxide.

It was found that cuprous oxide is readily peptized by concentrated ammonia water, or by ammonium sulphate in the presence of diluted ammonia water.

Furthermore it was found that an ammoniacal cupric solution could be decolorized by metallic copper only upon adding concentrated ammonia or ammonium sulphate.

Concentrated ammonia water or ammonium sulphate in the presence of diluted ammonia water evidently prevents the coating of metallic copper by a film of cuprous oxide, or peptizes the film if formed. Such a film would explain the incomplete reduction of the cupric solution, and, forming on the cathode, would, where broken through, give rise to a mass of relatively large, non-adherent crystals.

Procedure

A stock solution was prepared by dissolving 25 grams of the pentahydrate of cupric sulphate and 60 c.c. of concentrated ammonia water in sufficient water to make a liter of solution. A 100 c.c. portion of this solution was electrolyzed for 20 minutes at a current density of 6 milliamperes per square centimeter, using copper electrodes. A dense, bright, adherent, relatively smooth, and therefore good, deposit was obtained. The electrolysis was discontinued, but the electrodes were allowed to remain in the bath over night. The electrodes were then replaced by fresh ones. The solution was again electrolyzed, and after 20 minutes a coarse, non-adherent mass was observed. A good, fresh electrolyte was also converted into a bad one by allowing a strip of copper to stand in it for three hours, or by adding a centi-

gram of cuprous oxide. The addition of two grams of ammonium sulphate, or of an excess of concentrated ammonia, to the unsatisfactory bath resulted in a good deposit.

Several attempts were made to decolorize the slightly ammoniacal stock electrolyte by means of copper in the absence of air. The solution, however, remained dark blue indefinitely. But upon adding concentrated ammonia or ammonium sulphate to the solution it was promptly decolorized by the metallic copper.

If a film of cuprous oxide is responsible for the bad deposits, and for making it impossible to decolorize the stock solution by means of copper, it was to be expected that cuprous oxide would be peptized by concentrated ammonia water, or by ammonium sulphate, but not by diluted ammonia. It was found that the oxide was readily dissolved in concentrated ammonia water. Diluted ammonia water, or ammonium sulphate separately, were found to be without effect. But when ammonium sulphate was added to a slightly ammoniacal suspension of cuprous oxide the liquid rapidly became clear and colorless.

Summary

1. By electrolyzing a cupric ammonia complex a relatively dense, smooth, adherent, i.e., good deposit is obtained.

2. If metallic copper or cuprous oxide is dissolved in the ammoniacal cupric solution the deposit obtained consists of a thick, coarse, non-adherent mass of relatively large copper crystals.

3. The addition of concentrated ammonia water, or of ammonium sulphate to this now unsatisfactory electrolyte results in a good deposit upon further electrolysis.

4. A cuprous oxide film on the cathode is apparently responsible for the unsatisfactory deposit. Where this film is broken there grow loose crystals of copper.

5. An electrolyte from which an unsatisfactory deposit is obtained is one which does not peptize cuprous oxide.

6. Cuprous oxide is peptized by concentrated ammonia, or by ammonium sulphate in the presence of a small amount of ammonia.

7. The cuprous oxide film formed on copper added to a slightly ammoniacal cupric solution prevents the decolorization of the solution. The addition of concentrated ammonia or of ammonium sulphate peptizes the oxide, and the solution is decolorized.

Acknowledgment

Dickinson College,
Carlisle, Pa.

POLYMERIZATION AND DECOMPOSITION OF ACETYLENE HYDROCARBONS*

BY GUSTAV EGLOFF, C. D. LOWRY, JR., AND RAYMOND E. SCHAAD

Few fields in hydrocarbon chemistry offer the variety and the interest presented by the reactions of polymerization and decomposition of the acetylene hydrocarbons. The many products include gases, aliphatic and aromatic liquids, tars, and solids of unusual properties. There is variety too, in the means used to cause reaction, which include heat, chemical reagents, detonants, electric discharge, alpha particles, cathode rays, light, and electro-magnetic fields.

The interest in these reactions lies in part in their variability under changing experimental conditions. A single method of excitation, depending upon the conditions under which it is employed, may give rise to a gas, a low-boiling liquid, or an infusible solid. The elucidation of the mechanisms by which products so varied come from a single substance is a study of compelling interest. Attention is drawn to these reactions, moreover, by their commercial significance. Acetylenes have been proposed—and to some extent used—as a source of carbon, aromatic hydrocarbons, drying oils, synthetic rubber, and porous adsorbents.

Reactions of polymerization and decomposition are considered together for two reasons. As in the case of hydrocarbons of other series, changes of both types may be produced by the same agencies, and they often occur simultaneously.

Almost exclusively the investigations recorded concern acetylene itself. Only a few of the higher members of the series have been studied. This is understandable, as acetylene is readily obtained and there is hope of obtaining useful substances from it, while its homologs, even in the laboratory, are rarities.

I. Acetylene

A. *Introduction.*

The outstanding properties of acetylene are its unsaturation and its endothermic character. To its unsaturation, enabling it to add to itself, or to other substances, may be attributed its ability to form simple and complex polymers. Its endothermic character tenders it unstable, so that violent excitation, particularly at somewhat elevated pressure, will cause it to revert to its elements, sometimes with explosive violence.

Acetylene may be converted into polymers of comparatively simple structure by combination of two, three or four molecules, under the action of chemical reagents or the silent discharge, but only if reaction is carried out

under careful control. Uncontrolled polymerization goes much farther, heat producing aromatic liquids, and high-boiling tars, while the electric discharge, cathode rays, alpha particles, and light give rise to solid substances.

When fairly high temperature—1000° or above—is used, polymerization is negligible and acetylene breaks down to give carbon, hydrogen and methane. At still higher temperatures, for example in the electric arc, acetylene is more stable, and is formed in considerable proportion from methane or from carbon and hydrogen. The calculations of Francis and Kleinschmidt[69] indicate, however, that "it never becomes stable with respect to its elements." Before a temperature is reached at which no decomposition to carbon and hydrogen would occur, the hydrogen becomes monatomic and the equilibrium changes.

Catalysts reduce the temperature at which acetylene undergoes reaction. Some catalysts favor polymerization, while others change the predominant reaction at moderate temperatures from polymerization to decomposition. Metals are the substances which have been most used as contact agents.

B. *Action of Heat.*

The action of heat on acetylene at moderate temperatures—from approximately 300° to 800°—causes primarily polymerization to complex mixtures made up largely of aromatic hydrocarbons. Hydrogen, olefins and paraffins form to some extent, particularly in the upper portion of this temperature range. Below 800° decomposition is insignificant, but above this temperature it is the main reaction, and above 1000° almost the exclusive one. Carbon and hydrogen and some methane are produced. At 1200°-1300° acetylene decomposes completely;[20] at 1700° a trace of acetylene exists in equilibrium with carbon and hydrogen; at 2700° 3 percent, and at arc temperatures 7–8 percent of acetylene is present with hydrogen, methane and ethane.[167,32,166]

Notable are the yields of liquid products that can be obtained by pyrolysis of acetylene, which reach 70 to 99 percent of the hydrocarbon converted. Often 1/3 to 1/2 of the liquid is benzene. The list of substances which have been identified in these liquid tars is surprisingly long. R. Meyer[139-143] and his co-workers have reported the following:—hexene, benzene, toluene, ortho-, meta- and para-xylene, styrene, pseudocumene, mesitylene, indene, hydrindene, naphthalene, tetrahydronaphthalene, α- and β-methylnaphthalene, 1,4-dimethyl-naphthalene, diphenyl, acenaphthene, fluorene, anthracene, phenanthrene, purene, chrysene and fluoranthene.

Other workers have found dihydroanthracene in the products of non-catalytic pyrolysis, while the tar obtained in the presence of copper includes octylene, ethylbenzene, trimethylbenzene, ethyltoluene, propylbenzene, ethylnaphthalene, diethylnaphthalene, and methylstyrene.

In the gaseous products of acetylene decomposition, it has been mentioned that hydrogen and usually methane are present. Carbon almost invariably deposits in the apparatus. Ethane has in some cases been identified, and there have been frequent indefinite reports of "unsaturated and paraffin hydrocarbons."

In much of the work on the pyrolysis of acetylene the hydrocarbon has been passed through empty tubes. Sometimes the tubes were packed with activated carbon, which appears to promote smoother reaction and avoids sudden decomposition, though making no significant change in the character or yield of products. Refractory materials, such as firebrick or pieces of porous earthenware, are of some value as tube packing, particularly after becoming coated with carbon from acetylene decomposition, as this carbon appears to assist smooth reaction to liquid products.

Of pronounced catalytic activity are a number of metals. Copper is the most interesting, as it both reduces the temperature at which polymerization begins and changes its course, so that in place of low-boiling aromatic hydrocarbons there is produced mainly a high-molecular weight, fluffy brown solid, cuprene. Nickel and platinum are predominantly decomposition and hydrogenation catalysts, causing change at temperatures much below those necessary for reaction in their absence, and producing large formation of carbon and hydrogen and small amounts of polymerized products. Cobalt and iron have similar, though less pronounced action. They tend to cause breakdown to carbon and hydrogen, but do not prevent polymerization to liquid products. Manganese also furthers decomposition of acetylene. Finely divided iron, nickel, cobalt, and platinum are sufficiently reactive to initiate reaction at ordinary temperatures, and by passage of acetylene over them they soon become incandescent.

Many other metals, when in contact with acetylene at elevated temperatures, produce some carbonization, but they have not been studied to a sufficient extent to allow definite conclusions regarding their action to be drawn. Acetylide formation occurs with many metals as an accompaniment of decomposition reactions, and one cannot always distinguish between decomposition of acetylene by catalytic action of the metal and decomposition of an acetylide following reaction of the hydrocarbon with the metal.

Since both the polymerization and decomposition of acetylene are exothermic, care must be taken that the heat produced in its pyrolysis is dissipated, lest explosions occur, or the reaction get out of control. In the experimental work, rates of flow are adjusted to avoid decomposition, and often the hydrocarbon is diluted with non-reactive gases for smooth operation. Studies have also been made using a catalyst suspended in oil, for better temperature control.

Reaction Mechanism.—The simplest acetylene polymerization is the combination of two molecules to form vinylacetylene. This reaction was first reported by Mignonac and Saint Aunay[144] in work using the silent discharge at low temperature, and the product isolated and characterized by Nieuwland, Calcott, Downing and Carter.[158] Both groups assume, as first step, an activation of acetylene, Mignonac and St. Aunay supposing this to cause a loosening of the bond holding one hydrogen atom, so that the active molecule adds as H and $-C \equiv CH$ to the triple bond of a second acetylene. The later workers represent the activated molecule as $H_2C = C =$, and suppose a second molecule to add to it as H and $-C \equiv CH$ to form vinylacetylene.

By Nieuwland and coworkers further reaction is represented as addition of active acetylene to vinylacetylene to give divinyl acetylene, or activation of vinylacetylene itself and its doubling to a tetramer of acetylene. Mignonac and St. Aunay postulate addition of activated acetylene to the double bond of vinyl acetylene to give either:

$$HC \equiv C - CH_2 - CH_2 - C \equiv CH \quad \text{or} \quad HC \equiv C - CH - C \equiv CH$$

Dipropargyl

$$CH_3$$

Methylpentadiine
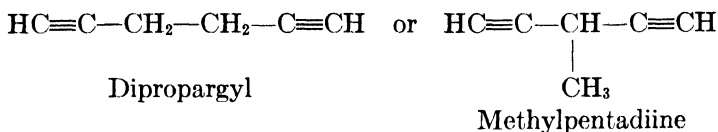
The formation of divinylacetylene, they state, is by way of addition of active divinylacetylene to acetylene.

In the silent discharge this addition process apparently continues until solid products are produced, as these solids are unsaturated, are able to absorb oxygen, and appear to be aliphatic in nature. In the action of alpha particles and light on acetylene, solids also form, but there appear to be no intermediate products. Lind and Schultze[128] believe that with alpha radiation a cluster of molecules around an ion is neutralized and at once goes to the final product.

These mechanisms do not cast much light upon the formation of aromatic hydrocarbons when acetylene is subjected to heat. No one has as yet formed aromatics by continuation of the low temperature polymerizations whose first steps are known; nor have any substances intermediate in aromatic formation been identified.

Berthelot[11,12,14] postulated that three molecules of acetylene combine in some way to form benzene, (he gave no intermediate steps) and that the higher aromatics form by successive additions of acetylene molecules to benzene accompanied in some cases by dehydrogenation. Thus, benzene and acetylene would form styrene, and addition of another acetylene molecule and loss of hydrogen form naphthalene. Benzene and styrene would unite and lose hydrogen to form anthracene. Continuation of such a process perhaps gives the solid product of aromatic nature, cuprene, that forms when polymerization occurs in the presence of copper. Activation of acetylene molecules very likely precedes these additions, and Berl and Hofman[8] suppose the formation of radicals during aromatic formation.

To account for the formation of methane, Bone and Coward[31] postulate that the first change is fission of acetylene to $\equiv CH$ radicals, which then add hydrogen to form methane. An alternative mode of formation would be recombination of carbon and hydrogen from acetylene decomposition. The amounts of methane found by Bone and Coward are far higher, however, than can exist in equilibrium with hydrogen and carbon at the temperatures employed. This rules out a direct synthesis and appears to support the radical hypothesis. Further evidence against formation from carbon and hydrogen is the fact that in the work of Bone and Jerdan[32] the yield of methane dropped with time of exposure. Hurd[93] however, criticizes the assumption of radicals as follows:

"The main objection to Bone's mechanism postulating HC≡ is that a split of C≡C requires so much more energy than a C—H split. For a scission of C—C it is estimated at 71 kg. cal; C—H is 90; C=C is 124 and C≡ is much greater. But for C=C to split *one* of the two bonds, giving C—C, would seemingly require no more energy than for C—C to split into C— and C—. Similarly, one of the three bonds of acetylene could split and give rise to polymerization. In the polymer, assuming it is vinylacetylene, there is a double bond. If one of the bonds of the double bond is opened for another polymerization, it could be assumed that ethylidene-diacetylene, CH_3—CH (C≡CH)$_2$, might arise. Now there is a single bonded methyl group which could reasonably be detached as methane. If this occurred, everything else is a C—H scission which would give rise to carbon and hydrogen. This is something akin to Berthelot's interpretation."

Ethylene and ethane no doubt form by direct hydrogenation of acetylene. The cokey deposits sometimes formed are perhaps the result of successive polymerizations and dehydrogenations as postulated by Berthelot, but that this sort of change is the sole means by which carbon forms is not likely to be the case, as an equilibrium condition exists between carbon, hydrogen and acetylene.

1. Without Catalysts

The first experiments on the action of heat on acetylene were carried out by Berthelot. His work on acetylene is a particularly important part of his hydrocarbon investigations, as he assumed acetylene as an intermediate product in the pyrolysis of practically all the hydrocarbons which he studied. In his early experiments,[11,12,14] he heated acetylene to the softening point of glass in a bent tube, one end of which was closed by immersion in mercury. He reported slow decrease in volume and formation of tarry products. At the end of half an hour 97 percent of the original acetylene had disappeared, being converted almost entirely into a liquid, which was mainly benzene, but contained some styrene, naphthalene, anthracene, and unidentified fluorescent hydrocarbons. A little free carbon and a corresponding amount of hydrogen were also produced.

He also found that when passed through a porcelain tube at bright red heat, the change in acetylene was almost entirely decomposition. At this temperature, acetylene decomposed more readily in the presence of carbon than in its absence, and in either case gave largely carbon and hydrogen. Minor products were ethylene, methane, naphthalene, and tar. To explain the separation of carbon, Berthelot assumed that the decomposition of acetylene at red heat consisted of a progressive polymerization, hydrogen splitting off in the process until only carbon remained. When he further increased the temperature,[18,19] and decomposed acetylene by exposure in a quartz tube for one hour at 1307° to 1325°, followed by sudden cooling of the tube to ordinary temperature by immersion in water, the tube was found to contain a brilliant form of carbon, and the gas consisted mainly of hydrogen, mixed with small amounts of methane and carbon monoxide. (Apparently the acetylene was slightly impure).

By carrying out his experiments on a larger scale, Berthelot[18] obtained a greater quantity of the yellow liquid product. It contained 50 percent benzene and 20 percent styrene. Above styrene, a 210°-250° fraction came over in which naphthalene was present. The distillate obtained between 250° and 340°, which was highly fluorescent, was thought to contain hydrogenated anthracene or ditolyl. From this liquid a few crystals of anthracene separated.

The work of Berthelot indicated definitely the predominant trend in the action of heat on acetylene to be toward the production of aromatic hydrocarbons by polymerization at moderate temperatures, and toward carbon and hydrogen at more elevated temperatures.

Subsequent researches will not be taken up in strictly chronological order, but a number of the more recent investigations are placed first to give at the onset a survey of present knowledge in this field.

Pease[162] found that the lowest temperature at which acetylene conversion occurred at a significant rate was about 400°, and produced evidence that polymerization of this hydrocarbon is a bimolecular and homogeneous reaction.

On seven minutes' exposure at 400° reaction was detected by a white mist appearing in the effluent gas, accompanied by an "odor similar to that of carburetted water gas." The reaction accelerated notably as the temperature was raised, so that the mist gave place to a mobile brown liquid. The product was a complex mixture with a wide range of volatility. "It contained benzene along with other volatile hydrocarbons subject to attack by concentrated sulfuric acid. . . . Very little permanent gas was formed until the temperature approached 550°, even though more than half of the acetylene might react." The gas produced was hydrogen with small quantities of methane and ethane. "At 600° regular flashing (a sudden luminous decomposition throughout the mass of the gas) began at higher flow rates, though it was possible to carry the reaction to 650° with low flow rates. In this high temperature range, finely divided carbon carried out of the tube."

Pease reported the polymerization bimolecular, because of retardation of the reaction when nitrogen was mixed with the acetylene before entrance into the heated tube. The fact that the rate of change was decreased by filling the reaction tube with glass packing was taken as evidence that the reaction was homogeneous rather than a wall reaction.

Bone and Coward[31] reported that,

1. At moderate temperatures acetylene shows a strong tendency to polymerize, maximum reaction occurring at 600°-700°, and decreasing above this temperature, so that little polymerization is found at 1000°.

2. At low temperatures acetylene tends to combine with hydrogen, but this is insignificant above 1000°.

3. At 800° and higher, the primary change is dissolution, and considerable amounts of methane form, which is attributed to hydrogenation of ≡CH residues initially formed.

Bone and Coward either circulated the gas through a porcelain tube surrounded by an annular space containing hydrogen to promote even heating, or passed it into or through a glass tube packed with porcelain fragments. At 480°-500° with an exposure of 20 hours about 82 percent of the acetylene reacted. Of this 48 percent polymerized, 39 percent decomposed into carbon and hydrogen, and the remainder was converted into methane, ethane, and ethylene. In an experiment of eight and one-half hours' duration at 650°, 60 percent by weight of the acetylene changed was polymerized, 30 percent resolved into carbon and hydrogen, and the remaining 10 percent appeared as methane, ethane, and ethylene.

At 800°, because of the rapidity of decomposition, the circulation method was abandoned, and the hydrocarbon simply passed into the heated tube, in which it was allowed to remain from 1 to 60 minutes. "Except when the gas was largely diluted with nitrogen or hydrogen, it always 'flashed' as soon as it entered the hot vacuous tube, so that its temperature momentarily must have been considerably higher than was recorded by the pyrometer." Although the greater part of the acetylene was thought to be decomposed during the flashing, the appearance of a mist in the condenser showed that polymerization still occurred. Much methane was formed. Methane was also produced in high yield when acetylene was heated with hydrogen at 800°. This was taken as proof of the suggested mechanism involving hydrogenation of $\equiv$CH radicals to form methane.

At temperatures of 1100° to 1150° polymerization diminished, while formation of carbon and hydrogen increased. Methane was also found at these temperatures. A summary of the results at the higher temperatures is given in Table I.

TABLE I

Decomposition of Acetylene

(Bone and Coward)

Temperature	600°	1000°	1150°
Polymerization, % of acetylene used	19	7.5	5
Analysis of gaseous products, %			
by volume acetylene	1.35	1.55	0
Ethylene	0.45	2.60	0
Ethane	0.50	0	0
Methane	32.40	36.00	23.45
Hydrogen	63.50	59.85	76.55

When Bone and Jerdan[34] admitted acetylene to an exhausted porcelain tube maintained at 1150°, the gas decomposed so rapidly that after an exposure of one minute not more than ten percent remained, and only a mere trace was present after five minutes. During the early stages of reaction considerable quantities of methane formed, which, as the decomposition progressed, was slowly but never completely resolved into its elements. Neither benzene nor ethylene formed at any stage of the decomposition; nor were there any gaseous products besides hydrogen and methane. Carbon

was liberated, at first in a form resembling lampblack, but later depositing on the inner surface of the tube in a form resembling gas carbon.

The highest yield of liquid products that has been reported is that of Berl and Hofmann,[8] who obtained a 98.8% conversion. The acetylene was saturated with water at 60-65° (the partial pressure of water was 150 mm.) and passed at 740° with a time of 4 seconds through a glass tube mounted in a copper block and filled with porcelain beads. The contact mass became coated with carbon, and held its effectiveness so that the yield did not drop during the run. The liquid was made up principally of aromatic hydrocarbons and higher acetylenes. The effect of the water was believed due to its reaction to form carbon dioxide, this reaction taking up part of the energy liberated by the decomposing acetylene.

The most extensive work on acetylene pyrolysis has been done by Meyer and his co-workers. To them we owe the identification of the many substances produced by polymerization. They worked on a sufficiently large scale to make extensive separation of products. In their first studies, intended primarily to determine whether the compounds in the pyrolytic tar from acetylene were those of coal tar, Meyer[139] repeated Berthelot's experiments with increased amounts of material, circulating acetylene at the rate of 40 liters per hour through two vertical, electrically heated, porcelain tubes, the first kept at 640° to 650° and the second at 800°. The hydrocarbon was about 1.1 minute in each heating tube. Before pyrolysis the acetylene was diluted with an equal volume of hydrogen, as otherwise it flashed and deposited carbon. After flowing through the heated tubes, the gaseous product, which contained a considerable proportion of methane, was used to dilute further quantities of acetylene.

The tar yield was about 63 percent of the acetylene converted, the remainder forming carbon, hydrogen and methane. The tar from the first tube was rich in light oils and that from the second in high-boiling hydrocarbons. The tars were submitted to repeated fractionation and crystallization and unsaturated hydrocarbons removed by bromine water. In the final product, benzene formed about 20%, toluene, which Berthelot did not find, was definitely identified, but xylenes were not proven. The fraction boiling from 150° to 200° contained indene. Steam distillation of the portion boiling between 200° and 300° yielded naphthalene, diphenyl and fluorene. From the 300° to 450° fraction small amounts of anthracene together with pyrene and chrysene were obtained.

To increase the amounts of tar, Meyer and Tanzen[143] used a more elaborate apparatus consisting of three vertical tubes of "Marquardt Mass" connected in series as to gas flow and heated electrically to 600°, 650°, and 800°, respectively. The yields of tar with this equipment varied from 27 to 57 percent of the acetylene treated. In the tar, in addition to the substances which Meyer had previously isolated, styrene, acenaphthene, and phenanthrene were identified, the first by conversion into its dibromide, and the others by their picrates. From the first runnings of the tar a hydrocarbon was isolated which boiled at 70° and whose analysis, density, vapor density and index of

refraction were identical with the constants of "hexene" obtained from mannite, which was probably a mixture of 1-hexene and 2-hexene.

Hoping to find other benzene homologs besides toluene in the lower boiling products from acetylene, Meyer and Fricke[140] systematically distilled the part of the tar from the previous investigation boiling between 50° and 150°. A fraction, which after removal of styrene boiled at 138°-139.5°, was proved to contain m- and p-xylene. The presence of o-xylene and ethylbenzene was suspected, but they could not be identified. From the fractions of the tar boiling between 150° to 250° and 250° to 350°, α- and β-methylnaphthalene, and diphenyl were isolated, together with small quantities of 1,4-dimethylnaphthalene. All of these were identified by their picrates. A fraction boiling between 193° and 206° from which a picrate could not be prepared, gave analytical values corresponding approximately to tetrahydronaphthalene and on oxidation with potassium permanganate and sulfuric acid yielded phthalic acid.

R. Meyer and W. Meyer,[141] in extending the work of Meyer and Tanzen, increased the dilution of the acetylene with hydrogen and held the temperature of the first heating tube to 550°, that of the second about 630°, and of the third at 850° to 900°. As in the earlier work, benzene, toluene and m- and p-xylene were identified, while in addition the presence of o-xylene was proved, and in higher boiling fractions pseudocumene, mesitylene, hydrindene and fluoranthene.

Meyer and Taeger[142] investigated a mixture of picrates obtained from the constituents of acetylene tar boiling above 300°. When decomposed with aqueous ammonia on the water bath this mixture gave a hydrocarbon tar boiling between 100° and 345°. From the fraction boiling up to 260°, fluorene, acenaphthene, anthracene, phenanthrene, pyrene, and fluoranthene were isolated. From the fraction 260° to 345° a small amount of picrate, melting at 231°, gave a hydrocarbon of empirical formula $C_{17}H_{10}$.

In the Presence of Added Carbonaceous Materials.

Many investigators who have carried out the heat treatment of acetylene in the presence of carbon, especially activated charcoal, claim advantages from the addition of carbonaceous material. When acetylene is pyrolyzed, however, carbon is almost always present as a reaction product, so that it is difficult to distinguish the exact effect of the added carbon. While some state that activated charcoal has a distinct action, others believe it to be effective only after becoming coated with carbon from acetylene decomposition, and find packing of other materials to be equally valuable.

Zelinsky and Kasansky[212,213] claimed that packing tubes in which acetylene was pyrolyzed with activated charcoal made possible the use of higher temperatures than could otherwise be employed without risk of flashing or explosion. It was thus possible to operate at the optimum temperature for polymerization, 600°-650°, which was difficult in the absence of the charcoal. The reaction was made smoother and less carbon deposited; no solid polymers formed and although there was some hydrogen in the final gases, no hydrogenation of acetylene occurred; the products were more largely benzene.

In the experiments of Zelinsky and Kasansky the gas was passed through a Jena glass tube containing the charcoal at temperatures up to 650°. The time allowed for reactions was 27 to 40 seconds. When the temperature of the heating tube reached 450°, white vapors appeared in the condenser, and became yellow and more dense as the temperature was increased. At 550° oil formed in the end of the tube and a dense fog filled the receiver. At 580°-600° the tar yield was 15 percent of the acetylene passed through the tube. At 620° to 630° with the same initial gas velocity the tar fog disappeared completely, liquid condensate flowed slowly into the receiver, and the yield was approximately 45 percent. The volume of exit gas was only 25 percent of that of the acetylene entering the apparatus, and about 60 percent of the gas was hydrocarbons heavier than acetylene. At 650° to 655° the yield of liquid condensate was 70 to 74 percent of the acetylene, and practically no gaseous products formed.

The condensate was a reddish brown tar of aromatic odor, and density varying from 0.911 (tar produced at 600°) to 0.995 (at 655°). A composite sample of density near the upper limit yielded 49 percent of light oil boiling below 170° (45 percent below 150°), 11.7 percent of middle oil boiling between 170° and 230°, 9.54 percent of heavy oil boiling from 230° to 270°, 21.2 percent of anthracene oil boiling above 270°, and 6.8 percent pitch. The light oil consisted mainly of benzene (35 percent of the tar), toluene (41 percent), para xylene (0.42 percent), and traces of styrene and indene. From the middle oil 6.7 percent of naphthalene and about 1 percent of fluorene were isolated. Anthracene was separated from the anthracene oil.

When these workers used an unfilled porcelain tube at 600° about 12.5 percent of the acetylene was converted into liquid condensation products during a run of 20 hours, and 2 percent of carbon deposited. Most of the hydrocarbon passed through unchanged. Over asbestos at 650° acetylene formed a thick, black, aromatic tar in yield of about 40 percent.

Kovache and Tricot[115] obtained yields of tar comparable to those of Zelinsky by passing acetylene downward through a vertical porcelain tube packed with activated charcoal, heated electrically at temperatures varied from 450° to 970°. The optimum temperature was about 650°. They reported, however, that charcoal did not aid the condensation until after it had been heated for some time. The condensation of acetylene to tar was effected just as well by a number of the other substances, including wood charcoal, coke, coke impregnated with aluminum oxide, porcelain, quartz, pumice or crushed brick, particularly if their surfaces were covered with a thin layer of carbon formed by decomposition of acetylene. The authors concluded therefore that activated charcoal does not have the specific catalytic action which Zelinsky attributed to it.

In their experiments, depending upon the conditions, 30 to 60 percent of the acetylene passed, or 33 to 76 percent of that which disappeared was converted into tar. A composite of these tars contained 28 percent of benzene, 1.5 percent of toluene, and 7.5 percent of anthracene.

Deposition of carbon, which eventually choked the reaction tube, could not be avoided by lowering the temperature, because when it was lowered enough to stop carbon deposition, polymerization also ceased.

When Kovache and Tricot passed acetylene through a horizontal silica tube packed with fragments of silica or porcelain and heated to 700°, 10 to 40 percent of the gas was converted into a tar of specific gravity 0.95 to 0.98 containing approximately 58 percent of benzene, 13 percent of naphthalene, and small quantities of toluene, dihydroanthracene, and pyrene. Part of the acetylene decomposed and produced carbon, which rapidly clogged the tube.

These workers then improved their apparatus by placing the tube vertically and introducing a water-cooled copper tube inside it, with an annular space of 2.5 to 3 mm. between the two, in order to condense the benzene and remove it as formed from the reaction zone. The yield of liquid tar was increased by this arrangement and the operation was made easier to control. From 70 to 90 percent of the acetylene passed, or about 90 percent of that consumed, was converted into a tar containing about 28 percent of benzene, 0.5 percent of toluene, and 4.3 percent of naphthalene. Rise in operating temperatures increased the velocity of the reaction and also the proportion of heavy hydrocarbons. Under the conditions used, the optimum temperature was 950°. At 1000° the liquid was black and viscous. The disadvantages of the hot-cold tube apparatus were the high heat losses due to the cold tube, and the gradual decrease in efficiency due to fouling of the hot tube by the formation of graphite. The results obtained were considered to preclude the possibility of a commercial synthesis of benzene by pyrolysis of acetylene.

Fischer, Bangert and Pichler[64] found that passage of acetylene over activated charcoal or over silica gel in a porcelain tube at 650° at first produced carbon, hydrogen, and methane. The carbon depositing on the charcoal or silica appeared, however, to be an effective catalyst for polymerization, and the production of liquid hydrocarbons soon began. After five hours of operation 70 percent of the acetylene was converted into tar which contained about equal amounts of light and heavy oils. At 600° the reaction products were the same as at 650°, but the yields were smaller.

The light oil, which boiled up to 150° (75% distilled below 110°), contained 70 percent of aromatic and 30 percent of unsaturated hydrocarbons, had an odor of benzene and was of a clear yellow color. The heavy oil was dark and opaque with a distinct odor of naphthalene. Ten percent of it distilled up to 150°, 50 percent came over to 230°, and solidified on cooling. The remainder was thin tar oil.

Work was done at 750° and 200 mm. mercury pressure, but the use of diminished pressure was said to have no significant advantage.

Dilution of acetylene with hydrogen and carbon dioxide favored light-oil formation and increased the life of the catalyst. Carbon dioxide also revivified the catalyst after use at 700°-720°. When an equi-volume mixture of acetylene and carbon dioxide passed through an empty tube at 600°, 70 percent of the acetylene was converted into liquids, of which about one-half was light oil.

Ika and Ogura[101] studied the polymerization of acetylene passing through a glass U-tube containing several active carbons at 600° and upwards. There was little difference in catalytic activity between activated charcoal, coke and coalite. No special relationship was found between the decolorizing ability and the catalytic action of the carbon, Coarse granular catalysts were most suitable as with fine carbon there was danger of local overheating in the reaction tube.

The optimum reaction temperature, as in the work of others, was 650° to 660°. Under these conditions 60 to 70 percent of the acetylene was converted into oily products containing 50 to 60 percent of light oil, which distilled below 150° and was composed mainly of benzene.

Other Researches.

Rousseau[179] reported the production of black diamond and graphite by decomposition of acetylene at temperatures approaching 3000°.

Haber and Oechelhäuser[82] found that when acetylene was passed into a porcelain tube at 620° the temperature rose immediately and remained at 638° to 645°. The products were largely liquid, consisting of about 40 percent of benzene; naphthalene was not observed; gaseous products equaled 4.2 percent of the acetylene, 3.2 percent being converted into ethylene.

On passing acetylene through a Jena glass tube which was heated gradually, Tiede and Jenisch[199] observed at about 440° the formation of a gray fog, which they took as an indication of the beginning of polymerization, together with a small separation of carbon on the walls of the tube. Raising the temperature increased the fog, and at about 540° the first oil drop appeared. At 600° about 31 percent by weight of the acetylene was converted into oil. Small amounts of paraffins, olefins, and hydrogen were present in the effluent gas which was largely unchanged acetylene.

Hilpert,[88] to form benzene, passed acetylene through a heated Jena glass tube filled with glass fragments. A tar fog appeared at 400°. At 500° a layer of carbon formed slowly on the glass and a tar was obtained containing small amounts of benzene and unidentified unsaturated hydrocarbons.

Sinkinson[196] found that the carbon deposited from decomposing acetylene upon two overlapped wires in a layer .0025 cm. thick was so cohesive that a considerable force was necessary to part the wires.

Walker[202] found that while acetylene was stable at 400°, at 450°, with a low gas velocity, it polymerized to a brown fluorescent liquid which appeared as minute drops in the cooler end of the heating tube. There was also a slight amount of decomposition. No polymerization was observed at this temperature when the gas flow was increased. Somewhat greater polymerization and some decomposition occurred at 550°, at the latter temperature 11 percent of the acetylene being decomposed. The residual gas contained 87.6 percent acetylene, 1.9 percent hydrogen, 7.8 percent ethylene, and traces of methane and ethane.

Fujio[73] passed purified acetylene into a glass or porcelain tube filled with pumice, clay, Japanese acid clay, or brick at 400° to 700°. The yield and

chemical nature of the tar produced varied with changes in temperature, rate of passage of acetylene, and the nature of the contact material. The maximum yield of tar, about 82 percent, was obtained by passing the gas over clay at 650°. It was made up almost entirely of aromatic hydrocarbons, including benzene and naphthalene.

When tubes of aluminum, copper, nickel, or iron, or iron coated internally with enamel, tin or iron sulfide were used instead of the glass tube the decomposition into carbon, hydrogen, and other gases was accelerated and was greater than the polymerization. In addition the tar thus produced differed from that obtained with glass, the fraction boiling between 100° and 250° being larger.

Constable[49] decomposed acetylene at a graphite surface supported on china clay rods, heated electrically to temperatures varying from 800° to 1200°, in order to study the catalytic properties of the carbon film.

Hague and Wheeler[83] produced oil and considerable quantities of soft carbon by passing acetylene downwardly through a vertical quartz tube at 600° to 750°. As shown by Table II, the maximum yield of liquid, 61.1 percent of the acetylene treated, was produced in the range 650° to 700°.

TABLE II

The Polymerization and Decomposition of Acetylene

(Hague and Wheeler)

Temp.	Yields in percent by weight of acetylene treated			Gas analyses, percent by volume				
	Total liquids	Benzene fraction	Carbon	Higher olefins	C_2H_2	C_2H_4	H_2	CH_4
600	30.8	—	—	0.8	53.2	4.2	27.9	8.3
650	61.1	26.4	9.7	1.2	29.5	6.9	34.0	23.0
700	61.1	24.8	16.7	1.2	2.4	10.4	43.8	37.1
750	46.7	18.3	22.1	0.2	0.7	8.8	50.1	37.5

Ipatiev[102] suggested the possibility of producing aromatic hydrocarbons commercially from acetylene from waste calcium carbide, which has no market value and must be destroyed. He stated that in a semi-manufacturing scale plant the Bayerische Stickstoffwerke obtained up to 65 percent of aromatics by passing acetylene through an electrically heated furnace containing carbon plates separated by clay plates impregnated with a catalyst, at a temperature of 600-650°.

Polymerization of acetylene by action of heat on the gas in the burner before it reached the orifice, followed by decomposition of the polymers in the flame was the cause assigned by Bullier[39] and Gaud[74] for carbon formation on acetylene burners.

Bradley and Parr[38] reported that acetylene was completely decomposed into its elements by contact with carbon at 725°.

Kennaway[112] found that by passing acetylene through a silica tube filled with pieces of porous plate at 700° to 920° a tar was produced, which could produce cancer in mice on application over a long period.

Acetylene has been proposed as a source of carbon by Salvadori.[189]

Patents.

Gros[79] claimed to produce a mixture of aromatic hydrocarbons from acetylene or gaseous mixtures containing acetylene by passing the gas through a reaction vessel filled with pieces of retort carbon heated electrically to 500° to 700°. The carbon filling was said to have no catalytic action, but to prevent local increase of temperature, which might cause spontaneous decomposition of the acetylene. He stated that a temperature of about 500° was best suited to the production of benzene and toluene. In another patent[80] covering a similar process, he gives as an example heating a mixture of 50 percent acetylene and 50 percent hydrogen to 580° to produce a mixture of liquid hydrocarbons containing 38.1 percent benzene, 2.6 percent toluene, and 7.5 percent naphthalene.

Ylla-Conte,[205,207,208,209] patented an apparatus for producing benzene and other liquid hydrocarbons from acetylene by subjecting the gas to a temperature of 450° to 600° in large iron or steel vessels and circulating the gas through a refrigerating apparatus outside the reaction vessel to remove the benzene and liquid products formed. The uncondensed gas was injected into the reaction vessel to mix with the gas undergoing treatment and to prevent undue rise of temperature.

It was stated that once the process was started it was unnecessary to heat the acetylene, and the operation was continuous and automatic. By regulating the speed of circulation through the refrigerant it was possible to vary the quality of the products.

A number of patents have been taken out on the preparation of high-grade carbon black by decomposition of acetylene.[190] Hubau[92] explodes acetylene in steel vessels under a pressure of 2 to 5 atmospheres. Hostmann Steinbergsche Farbenfabriken Ges.[90] also ignite the gas under pressure. Frank[70] dilutes with carbon monoxide or carbon dioxide before decomposition. Berger and Wirth[7] also dilute the hydrocarbons.

Wheeler, McAulay and Francis[210] pyrolyze a variety of hydrocarbons and hydrocarbon mixtures, including acetylene, by passage in two or more stages, through a space heated to 1000°-1200°. The liquid products, which include benzene and its homologs and olefinic substances, are separated from the gases between treatments.

2. With Catalysts

A. *Metals.*

i. Cobalt, Copper, Iron, Nickel, Platinum

The course of acetylene pyrolysis is greatly changed by the presence of metals. Of particular importance is copper, which has strong polymerizing action and produces a characteristic solid, cuprene. Polymerizing action, it will be recalled, is possessed by a salt of copper, cuprous chloride, even at

room temperatures. Iron lowers the initial temperature of acetylene decomposition, and favors decomposition to carbon and hydrogen, though not excluding production of oils. Nickel aids decomposition to carbon and hydrogen and causes partial hydrogenation of the acetylene, as well as some polymerization, which may go as far as the production of a solid cuprene-like substance. Platinum is also a decomposition and hydrogenation catalyst, but loses its efficiency at high temperatures through becoming coated with carbon.

The effectiveness of cobalt is said to lie between that of nickel and of iron. The metal lowers the initial decomposition temperature of the hydrocarbon, giving rise both to carbon and hydrogen and to polymerized products. Pyrophoric iron, nickel or cobalt will become incandescent in a stream of acetylene, as will also finely divided platinum.

The metals are arranged alphabetically in two groups, first those of pronounced reactivity with which important results have been obtained—cobalt, copper, iron, nickel and platinum—and, second, those which have been subject to but little investigation, or have been found to have no pronounced effect on the course of the pyrolysis. Little effort is made to analyze the action of the metal, whether it should be classed as a catalytic agent, or be considered rather as a participant in a chemical reaction. With the five metals discussed in detail, there is, probably, true catalytic action. With some other metals, the change occurring is largely acetylide formation, and not catalysis. Acetylide formation is almost always accompanied by deposition of carbon, which is taken to indicate decomposition of the acetylene and to constitute justification for the inclusion of the results in this paper.

Cobalt.—Moissan and Moureu,[149,151] found that passage of a rapid current of acetylene over pyrophoric cobalt (prepared by reduction of the oxide at the lowest possible temperature) caused the metal to become incandescent. Carbon, hydrogen and a liquid hydrocarbon product rich in benzene were formed.

These investigators believed that the generation of heat was initiated by the energetic absorption of the acetylene by the porous reduced metal, and that the heat then acted on the acetylene to cause part of it to polymerize and part to decompose. When the acetylene was diluted with nitrogen, there was no incandescence, although the hydrocarbon was absorbed and slightly decomposed.

Sabatier and Senderens,[186,188] observed that finely divided cobalt had no action on acetylene or acetylene mixed with hydrogen at room temperature, but when exposed to the hydrocarbon at temperatures above 200° the metal became incandescent and the gas was almost completely decomposed. They considered the effectiveness of cobalt to be less than that of nickel and greater than that of iron. Greenish yellow liquids formed, resembling those obtained with nickel. These resembled natural petroleums, and their formation was used as the basis for an acetylene theory of petroleum formation. The gaseous products were largely hydrogen and ethane, with a trace of benzene, while the heating tube filled with a black material, consisting of carbon mixed with cobalt, containing a small amount of a fibrous hydrocarbon similar to cuprene.

Hodgkinson[89] also reported cobalt to induce reaction when heated in acetylene to about 200°. The metal became corroded and pitted, and quite brittle. Carburisation was greater and soot formation less when the gas was diluted with ammonia.

In the work of Tiede and Jenisch[199] cobalt caused separation of carbon from 380°, and oil formation at 480°.

Fischer, Peters, and Koch[66] produced complete decomposition of acetylene by passing it over cobalt at 300°. There was no liquid product and methane was the only substance identified.

Cobalt is used by the I. G. Farbenindustrie, A. G.[99] in the treatment of acetylene to produce lamp black.

Copper.—The main product of the action of heat on acetylene in the presence of copper (or its oxides) is a voluminous brown solid "cuprene." Oily products and gases are produced in smaller amount at the same time. The formation of cuprene has been frequently and extensively investigated. It is a polymer of indefinite composition, aromatic in nature, though of undetermined structure. A trace of oxygen seems to be required to initiate its formation.

Cuprene was first reported by Erdmann and Köthner[59] who found that a light brown, highly voluminous solid was formed by the action of acetylene at 230° upon cuprous oxide, or more slowly by action on finely divided copper. The passage of acetylene during 18 hours over one gram of cuprous oxide yielded 7 grams of this product, which occupied a space of nearly 300 cc. In addition, a black carbonaceous mass formed, and at "red heat (400°–500°C.)" carbon was deposited in graphitic form. Below 180° only liquid polymers formed.

Erdmann and Köthner considered the brown fluffy product to be a complex, non-explosive, copper acetylide of the formula $C_{44}H_{64}Cu_3$. When heated with an excess of zinc dust it yielded 20 percent by weight of an oil boiling between 190° and 250°, having an odor similar to that of Caucasian naphtha. If the mixture with zinc dust was heated to a higher temperature, aromatic hydrocarbons, including naphthalene, appeared in the distillate, while a portion which dissolved in caustic soda appeared to be cresol.

From experiments made by passing acetylene over heated copper oxide, Gooch and Baldwin[76] came to the conclusion that the "Kupferacetylen" obtained by Erdmann and Köthner[59] was not a copper acetylide but a hydrocarbon or hydrocarbons mixed with copper or an oxide of copper. The copper content of this product, they found, varied between 1.5 and 24.2 percent, and depended upon the conditions of the experiment. While they readily obtained it by the action of acetylene on either cuprous or cupric oxide, when a roll of copper gauze was carefully reduced in hydrogen, oxidized at one end in the outer portion of the flame of a Bunsen burner, and then exposed to a current of acetylene at 225° to 250°, it yielded the spongy product upon the oxidized end only. "These results go to show that, while metallic copper may, at comparatively high temperatures, induce the polymerization of

acetylene, it is an oxidizing action which, at moderately low temperatures, starts the formation of the peculiar derivatives under consideration."

When Alexander[1] passed dry acetylene over spongy copper contained in a tube which was heated slowly, the action started at about 225°. The copper began to swell, the effluent gas stream became slower, and drops of a heavy distillate with a petroleum-like odor separated in the cooler parts of the tube. The reaction proceeded smoothly between 240° and 250° but above 260° carbon deposited on the walls of the tube in a lustrous black layer. No gaseous products were formed at 240°-250°. A light brown cork-like mass eventually filled the entire tube. This mass contained two percent of copper, which was thought to be held mechanically, as treatment with hydrochloric acid containing ferric chloride lowered the copper content to 0.2 percent.

The most extensive investigations of the decomposition of acetylene in the presence of copper were made by Sabatier and Senderens.[180,181,182,188] They found that the admission of acetylene to copper, reduced from the oxide by hydrogen at low temperature, immediately caused a reaction even in the cold, manifested by a slight rise in the temperature of the metal and by a petroleum-like odor of the effluent gases. This reaction, which lasted for only an instant, was thought due to hydrogenation of acetylene by hydrogen adsorbed by the copper. When this brief reaction ceased the metal became cold. It did not occur with copper which had been reduced by carbon monoxide or by hydrogen at red heat.

If the temperature was raised above 180°, the copper turned brown, and the pressure decreased rapidly because of rapid polymerization of the acetylene. In the cooler part of the tube a colorless liquid deposited, consisting mainly of olefin hydrocarbons. Microscopic examinations of the copper showed no appreciable change in its structure. Prolonged action of acetylene at 180° to 250° caused the copper to swell, and form a yellowish brown mass composed of microscopic filaments, which filled the heating tube. This material, when compressed, resembled tinder, and was reported to consist of a non-volatile hydrocarbon mixed with about 1.5 percent of copper. The composition of this substance corresponded to the empirical formula $(C_7H_6)n$. Sabatier and Senderens suggested the name "cuprene" for this hydrocarbon on account of its method of formation.

Besides the formation of cuprene, there was condensation of greenish liquids which consisted of a mixture of unsaturated and aromatic hydrocarbons (benzene, styrene, etc.). The small amount of gas which left the heating tube had the following composition (percent by volume):

H_2	C_2H_6	C_2H_4	C_3H_6 and C_4H_8	C_2H_2
20.2	12.1	45.2	16.5	6.0

In the presence of copper sheet or wire the reaction was identical with that obtained over reduced copper. Well-cleaned copper when heated at 200° to 250° in a current of acetylene was covered by the same sort of brown layer, which became yellowish as its thickness increased. Some of the deposit

placed in a clean tube and heated at 180° to 250° in a current of acetylene, again swelled and filled the tube. After three or four such successive swellings in acetylene at 200°, a material was obtained which was no longer modified by further heating.

By suddenly conducting a current of acetylene over a column of reduced copper heated only in the middle portion, to about 250°, Sabatier and Senderens obtained a lively reaction which sometimes attained incandescence, producing cuprene mixed with carbon.

The formation of cuprene was regarded as "doubtless due to the formation of an unstable acetylide capable of reacting with acetylene to form a new condensed molecule, thus:

$$n\ C_2H_2 + n\ Cu = n\ C_2Cu + n\ H_2$$

$$\text{and}\quad n\ C_2Cu + 6n\ C_2H_2 = (C_7H_6)_{2n} + n\ Cu.$$
$$\text{cuprene}\quad\text{regenerated}$$
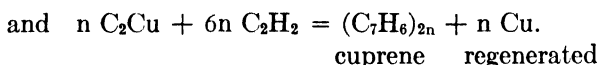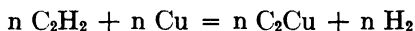
"The regenerated metal is capable of repeating the reaction indefinitely. The hydrogen set free combines with a portion of the acetylene over the copper to give chiefly ethylene hydrocarbons."

Hilpert[88] reported that passage of acetylene over heated copper immediately produced a brown deposit on the metal which in a short time obstructed the tube entirely, while a tar with unpleasant odor was formed in small quantities.

Comparative experiments in which Kaufmann and Schneider[110] conducted acetylene over reduced copper, cuprous oxide, cupric oxides, and a residue produced by heating anhydrous copper ferrocyanide in a current of air at 250° for 15 minutes, showed that the last gave the best yields of cuprene. Traces of a green oily liquid also deposited in the cooler parts of the heating tube.

The condensation product varied in color with the catalyst and the length of the heating. That obtained in the presence of the decomposed copper ferrocyanide was yellow to light brown, while that resulting with the other contact agents was dark brown to black. By further treatment with acetylene the dark material was converted into a lighter colored product containing less copper. If the time of heating was short, the product was loose and voluminous; but, if heating was continued six to eight hours, it was a cork-like solid. The empirical composition of the products obtained with different temperatures and catalysts varied between $(C_{11}H_{10})_x$ and $(C_{15}H_{10})_x$.

By working with very pure acetylene produced by the action of alcoholic potassium hydroxide on ethylene dibromide Kaufmann and Mohnhaupt[109] found that the conversion of acetylene into cuprene in the presence of reduced copper at 230° to 300° did not take place in the complete absence of oxygen. These investigators believed that cuprene formation was due to production of an intermediate additive compound of acetylene with cuprous or cupric oxide which immediately underwent pyrolysis. The acetylene released by the decomposition of the addition compound was considered to be particularly reactive, and consequently, to undergo reactions more profound than those involved in the pyrogenic changes of acetylene when heated alone. These

reactions were thought to lead through a series of intermediates to the inactive cuprene. The regenerated copper oxide was considered capable of adding acetylene as before.

A study of the cuprene showed that it did not absorb oxygen in the cold, halogenated with difficulty, and on oxidation with nitric acid formed mellitic acid. This indicated an aromatic nucleus. As to the remainder of its structure, its hydrogen content was too low for it to have saturated side chains, while the difficulty of bromination ruled out unsaturated side chains. A polycyclic aromatic structure was, therefore, most probable.

The solid product from action of the silent discharge on acetylene, somewhat similar to cuprene, in appearance, eagerly absorbed oxygen, and was thought from this and other properties to be essentially aliphatic in composition.

Schläpfer and Stadler[192] reported that the Elektrizitätswerk Lonza A.-G. prepared cuprene on a large scale by passing technical acetylene over copper at about 300°. The reaction was carried out in reaction vessels of several cubic meters capacity containing the finely divided metal. After air was expelled by acetylene, the apparatus was heated until the reaction began, which required a temperature of about 200°. The heat of reaction then caused the temperature to rise quickly to 250°–300°. At this temperature the operation was conducted for several days by continuously introducing acetylene, to which an inert gas had been added in order to prevent too energetic reaction. The acetylene produced 75 to 80 percent by weight of cuprene, 5.5 to 7 percent of tar, and 13 to 17 percent of gases.

The cuprene-tar was a greenish-blue liquid of specific gravity 0.878 to 0.910. Fractional distillation at atmospheric pressure up to 112°, then at 12 mm. to 170°, and finally at 0.3 to 0.5 mm. to 220°, followed by treatment of the fractions with sulfuric acid and bromine showed that the tar consisted mainly of aromatic hydrocarbons, with smaller quantities of olefins, and a small proportion of paraffin hydrocarbons boiling between 28° and 64° at 720 mm. The substances which Schläpfer and Stadler isolated from the tar were: hexylene, octylene, benzene, toluene, xylene, ethylbenzene, styrene, methylstyrene, trimethylbenzene, ethylmethylbenzene, propylbenzene, naphthalene, methylnaphthalene, ethylnaphthalene, diethylnaphthalene, anthracene, and an unidentified aromatic hydrocarbon $C_{10}H_{14}$.

Fischer and Peters[65] studied hydrogenation and polymerization of acetylene in mixture with hydrogen in the presence of a catalyst of copper precipitated on Kieselguhr suspended in paraffin oil.

Herzog[87] discussed the technical application and uses of cuprene. While full details of its manufacture have not been published, it is known that acetylene is passed over copper or bronze powder at 200-260° under pressure somewhat above atmospheric during action of the silent electric discharge. The temperature and pressure employed affect the properties of the product. Choking of the reaction tube is avoided in a patent of the Elektrizitätswerke Lonza[54] by a stirring mechanism. This company eliminates coking and obtains a purer product by dilution of the hydrocarbon with 5 to 15% nitrogen.

To reduce the space needed for reaction pure or dilute acetylene is introduced into a high-boiling liquid, such as stearic acid or paraffin oil, containing copper bronze at 250°-300°. The product is purified by washing with alkali or a solvent. The favorable action of a small amount of oxygen on cuprene formation, which has already been mentioned, is covered in a patent of Horwitz,[91] who increases yields by mixing acetylene with air, oxygen, or an oxygen supplying agent.

Many industrial uses of cuprene have been covered by patent and some of them no doubt put into practice. The utility of cuprene is based on its chemical indifference and physical structure. Herzog[87] gives a patent bibliography of this field. Among the uses he mentions are the replacement of cork in the linoleum industry, as a porous mass in acetylene cylinders, use as an absorbent for liquids, including fuels, disinfectants, and liquid oxygen explosives, as a rubber filler, as a constituent of dynamite, and of black powder.

Acetylene and benzol in the presence of aluminum chloride give a product much like cuprene, that has been patented by Consortium-Elektrochemische Industrie.[48]

In preparing solid high molecular polymerization products from acetylene for use as constituents of explosives Wohl[204] brought acetylene into contact with cupric oxide at about 230°.

The N. V. Electro-Zuurstof-en-Waterstoffabriek[157] states that high molecular weight products similar to cuprene are obtained by passing acetylene at 200° to 400° over copper, nickel, iron, or their oxides to which a small quantity of magnesium has been added. It is claimed that the cuprene may be used as a catalyst for the production of more cuprene by adding a small proportion of magnesium. "The product may be used to decolorize blue methylated spirit or to clean dirty water."

Tiede and Jenisch[199] observed that separation of carbon and formation of oil began at 310° when acetylene was passed over massive copper. At 600° the oil formed was equivalent to 14.5 percent by weight of the acetylene treated.

Erdmann[57] obtained graphite by slow decomposition of acetylene over copper at 400°-500°C.

Berl and Hofmann[8] found that at 580° copper caused carbon deposition and did not favor polymerization.

Deposition of a small amount of carbon was the only reaction which Hodgkinson[89] observed when acetylene was passed over copper heated at its melting point (1038°).

Iron.—Iron reduces the temperature at which acetylene decomposes. In its presence, acetylene is converted largely to carbon and hydrogen, although olefins and paraffins, particularly ethane, form simultaneously. Oily liquid products containing benzene, appear also, but only to a slight extent. Reaction may be so vigorous that the metal, originally at a low temperature, becomes incandescent. This is notably true if pyrophoric iron is used.

Berthelot[11,12,14] noted a reduction in initial temperature of acetylene decomposition when iron was present, and as products reported carbon, hy-

drogen (about 50 percent of the volume of the acetylene decomposed), and "empyreumatic hydrocarbons," which were said to differ from the products of the action of heat alone on acetylene. Acetylene mixed with an equal volume of nitrogen, carbon monoxide, methane, or ethane decomposed a little more slowly than did the undiluted gas.

Ramsay[169] passed a mixture of acetylene and hydrogen cyanide through a "bright-red-hot" iron tube and obtained a small quantity of distillate which, judged by its odor, contained benzene.

Moissan and Moureu[149,151] found that pyrophoric iron, prepared by reduction of the oxide with hydrogen at the lowest possible temperature, caused rapid reaction when brought in contact with acetylene at ordinary temperatures, so that the metal became incandescent. While part of the acetylene was converted into a liquid product rich in benzene, the greater part was split into carbon and hydrogen.

Sabatier and Senderens[186,188] found that the passage of acetylene, or mixtures of acetylene and small proportions of hydrogen, over iron obtained by reduction of ferric oxide, raised the metal from room temperature to incandescence and produced a black voluminous carbon in which iron was disseminated. A small amount of brownish liquid condensed, which was made up almost exclusively of aromatic hydrocarbons. The gaseous product contained hydrogen. If the entire tube containing the reduced iron was kept above 180°, considerable hydrogenation of acetylene took place, this occurring beyond the point in the tube at which the metal was incandescent. The exit gas contained 64 percent of hydrogen with smaller amounts of benzene, olefins and ethane.

Hilpert[88] reported that decomposition of acetylene began at 300° in the presence of finely powdered iron, and at 400° reaction was so rapid that separation of carbon soon obstructed the heating tube.

Hodgkinson[89] reported that when iron was heated in acetylene, either pure or diluted, the metal, if in moderately small pieces as wire, frequently glowed, the glow passing along the whole mass of metal employed. Carbon deposited on the iron and carburisation occurred. Some of the carbon formed from the acetylene entered the metal, and some of the iron entered the soot-like deposit formed upon it, so that this deposit was found to contain as much as three percent of iron. The carburising of iron by heating in acetylene was very rapid, especially above 800°, and appeared to reach a maximum just below 1000°. Photomicrographs of iron carburised by heating in acetylene for periods of one to three hours at 1050° showed distinct diffusion of carbon into metal. In acetylene diluted with ammonia, iron was carburised more rapidly than by acetylene alone, and the amount of extraneous carbon deposited was reduced.

Tiede and Jenisch[199] observed that carbon separation began at 400° and oil formation at 540° when acetylene was passed over iron. At 600° the yield of oil was only 0.6 percent by weight of the acetylene treated. Hydrogen and paraffins made up 99 percent of the effluent gas, which was free from olefins and contained only traces of undecomposed acetylene. Comparative experiments without the catalyst gave an oil yield of 16.8 percent, an effluent gas

containing 2.3 percent of hydrogen and paraffins, and 97.5 percent unchanged acetylene.

Bradley and Parr[38] found that acetylene was completely decomposed into its elements by contact with iron surfaces at 725°.

Rimarski and Konschak[176] produced almost complete decomposition of acetylene by slow passage at atmospheric pressure through an iron tube at 600° to 900°. No explosions occurred at 900° with pressures up to two atmospheres absolute.

Fischer, Peters, and Koch[66] found that when a mixture of 9 percent acetylene and 91 percent hydrogen was passed over iron a temperature of 300° to 340° was necessary to cause reaction. Both oil production and carbon deposition occurred.

Berl and Hofmann[8] reported that at about 580° iron was distinctly unfavorable to oil formation and caused heavy deposition of carbon.

Erdmann and Köthner[59] stated that when heated in acetylene iron acted somewhat like copper, aiding the conversion to oily hydrocarbons. As has been shown, most workers report that iron favors the formation of carbon and hydrogen.

The I. G. Farbenindustrie A. G.[99] claims the use of activated iron to treat acetylene for the preparation of lamp-black.

Nickel.—The effects of nickel on acetylene are summarized by Sabatier and Senderens[185,188] (referring largely to its action at 180°) as follows:—

1st. Rapid decomposition into carbon and hydrogen with polymerization to aromatic hydrocarbons.

2nd. Slow condensation into a solid hydrocarbon doubtless identical with cuprene.

3rd. Hydrogenation of the acetylene and of the aromatic hydrocarbons with product of unsaturated, and cyclo-aliphatic hydrocarbons.

"With a tube that is not externally heated, where the incandescence is intense and localized at a single point, the first effect is the greatest, the velocity of the gas rendering the subsequent hydrogenation unimportant."

Sabatier and Senderens[183] in their first work, found that finely divided reduced nickel increased in temperature when acetylene mixed with hydrogen was passed over it at ordinary temperature. Hydrogenation to ethane and ethylene was the predominant reaction, but a liquid product also formed consisting chiefly of paraffin hydrocarbons, with small amounts of higher olefins and benzene. The yield of liquid was greater the higher the temperature and the lower the proportion of hydrogen in the gas mixture. Low hydrogen percentage also increased the proportion of aromatic hydrocarbons in the product. With high acetylene concentrations the metal swelled up and became incandescent.

Moissan and Moureu[149,151] had earlier observed that the passage of acetylene at ordinary temperature over pyrophoric nickel (prepared by reduction of the oxide at the lowest possible temperature) caused the metal to become incandescent. The products were carbon, hydrogen and a liquid mixture rich in benzene.

In later publication Sabatier and Senderens[185,187,188] suggested that the incandescence might be due to an initial heating produced by combination of acetylene with hydrogen adsorbed by the metal, because there was no appreciable reaction below 180° when nickel was used from which hydrogen had been displaced by cooling the metal in nitrogen. About 180° a slow reaction began, but with slow gas flow there was no incandescence. At 250° reaction was more rapid, with both decomposition and hydrogenation of acetylene occurring. The largest constituent of the exit gas was ethylene, with smaller proportions of higher olefins, ethane, and aromatic vapors, but almost no hydrogen. The liquid products were reported to contain olefin, naphthene and aromatic hydrocarbons.

When a rapid current of acetylene was passed through a column of nickel of the same length at 200° to 250° the reaction was accompanied by incandescence, more free hydrogen and ethane, and less ethylene were formed. A small amount (15 cc.) of a deep-green fluorescent liquid was collected which contained hydroaromatic hydrocarbons. At the end of the experiments the heating tubes contained, besides carbon, a solid hydrocarbon resembling cuprene.

When nickel was kept between 180° and 300° for a long time in a slow current of acetylene, the metal swelled and became covered with a solid brown fibrous hydrocarbon similar in appearance to cuprene.

Charitschkow[43] conducted a mixture of acetylene and hydrogen over nickel shavings at 300°, and obtained a product that resembled naphtha. Five percent distilled to 150°, 14.5 percent between 150° and 200°, 29.25 percent between 200° and 270° and there remained a residue of 50.75 percent. All the fractions contained unsaturated hydrocarbons.

Tiede and Jenisch[199] found that carbon separation began at 360° and oil formation at 520° when acetylene was passed over nickel. At 600°, only 6.4 percent by weight of the acetylene was converted into oil. The rate of decomposition was made greater by increasing the fineness of division of the metal.

Hilpert[88] found decomposition of acetylene in the presence of finely divided nickel, to be increased when iron was also present. Above 300° carbon separation was so rapid as to fill the heating tube within a minute—a fact which made this catalyst useless for the preparation of benzene.

Hodgkinson[89] reported that when heated in acetylene, nickel became quite brittle and evidenced corrosion and pitting. Reaction was noted at about 200° and was rapid at 600°. The metal became covered with a soot-like deposit which contained 5 to 15 percent nickel. The metal was carburised more rapidly in a mixture of acetylene and ammonia than in acetylene alone, and the formation of soot was reduced.

Fischer and Peters[65] found hydrogenation from room temperature upwards when acetylene and hydrogen were passed over a catalyst of nickel precipitated on kieselguhr suspended in paraffin oil. At 250° a considerable amount of oily polymerization products was obtained.

The dehydrogenation of acetylene to lampblack by means of activated nickel has been claimed by the I. G. Farbenindustrie A.-G.[99]

Further experimentation with nickel is discussed in the section "Combinations of Metals."

Platinum.—Platinum, when finely divided, promotes the decomposition of acetylene to carbon and hydrogen. It is active even at room temperature, and when acetylene is passed over it becomes incandescent. The coating of the metal with carbon causes its influence to become less as the temperature rises, so that at 600° the reactions found are almost identical with those obtained with heat alone, except that there is a somewhat lower yield of oily products and a pronounced hydrogenation of acetylene through catalysis by the metal.

Moissan and Moureau[149,151] reported that a rapid passage of acetylene over platinum black, spongy platinum, or platinized asbestos at ordinary temperature caused incandescence. The products of the reaction consisted of carbon, hydrogen, and a liquid rich in benzene. If the acetylene was diluted, no incandescence occurred, but slow carbonization and liberation of hydrogen occurred.

Sabatier and Senderens[181,186,188] found that finely divided platinum-black had no action on pure acetylene at ordinary temperature, but that at 150° it caused rapid decomposition to carbon and hydrogen. The heat evolved brought the metal to incandescence, accelerating the decomposition, and caused the polymerization of much of the remaining acetylene into benzene, styrene, and reduction products of naphthalene and anthracene. The hydrogen formed reduced part of the acetylene to ethane and ethylene.

When a mixture of hydrogen and acetylene was passed over the platinum at room temperature, reduction to ethane and ethylene occurred; at 180° higher hydrocarbons, liquid and gaseous, were produced.[184]

Schützenberger[194] also reported that when platinum sponge is heated in a current of acetylene it becomes incandescent, the hydrocarbon is decomposed, and the metal swells and changes into a very finely divided and voluminous black powder containing considerable carbon.

Lewes[117] found that upon being passed through a platinum tube heated to 1000° acetylene yielded a mixture of gases of the following composition: acetylene 25.95%, other unsaturated hydrocarbons (chiefly ethylene, with some benzene vapor) 61.97%, saturated hydrocarbons 3.21%, carbon monoxide 1.01%, oxygen 0.38%, hydrogen 1.50%, nitrogen 5.98%. Each 100 cc. of gas treated yielded 0.095 gram of oil and 0.018 gram of carbon.

When Grehant[77] exposed acetylene in a firedamp eudiometer to a platinum spiral heated electrically to bright redness, it inflamed and deposited carbon.

Zelinsky and Kasansky[213] observed that no reaction occurred when acetylene was passed over platinized asbestos at ordinary temperature, but marked formation of liquid product began at 300°, and vigorous action occurred at 650°, forming a transparent bright yellow aromatic tar in yield of 45 to 50 percent. Forty-five percent of the tar distilled below 150°.

ii. Other Metals

Below are summarized the investigations which have been made on the decomposition of acetylene in the presence of other metals. The metals are taken up in alphabetical order.

Aluminum.—Kusnetsov[116] showed that when acetylene was passed over finely divided aluminum, heated nearly to its melting point (m.p. 659°) it decomposed almost completely into carbon and hydrogen, with formation of a small quantity of aluminum carbide. In similar experiments Durand[55] formed a carbonaceous mass which obstructed the reaction tube.

When Hilpert[88] passed acetylene over aluminum at 400° in a Jena glass tube, pine-tree shaped deposits of carbon formed at first but did not increase in size as reaction went on. As the temperature was increased the aluminum became black. A small quantity of tar formed which was like that obtained in the same tube when packed with glass fragments.

Hodgkinson[89] stated that the separation of a small amount of carbon was the only evidence of reaction when acetylene was passed over aluminum heated to its melting point.

Beryllium.—Durand[55] passed pure dry acetylene over powdered crystalline beryllium contained in a heated glass tube, and found that at about 450° the metal became black, due to a deposit of carbon, some polymerization occurred, and beryllium acetylide was formed.

Cadmium.—Cadmium acetylide mixed with carbon formed when Durand[55] passed acetylene over cadmium filings heated at about 500°.

Hodgkinson[89] reported that when heated to its melting point (321°) in a current of acetylene, cadmium did not change in physical state. A small amount of carbon deposited on the metal, and a greater amount combined with it.

Gold.—Durand[55] found that passage of acetylene over finely divided gold heated to 500° caused deposition of carbon on the metal. There was no evidence of acetylide formation.

Lead.—Carbon deposited when Hilpert[88] passed a slow stream of acetylene into molten lead (m. p. 327°). No benzene was formed even at 500°. Hodgkinson[89] confirmed this result.

Lithium.—Tiede and Jenisch[199] found that acetylene reacted rapidly with heated lithium forming acetylide and hydrogen. Marked separation of carbon also occurred.

Magnesium.—Berthelot[10] reported that an acetylide of magnesium formed when acetylene was passed over heated magnesium.

By cautiously heating powdered magnesium in a current of acetylene Moissan[150] obtained a mixture of carbon and an impure magnesium carbide. Keiser and McMaster[111] reported that when acetylene was passed over heated magnesium a black residue was produced which, with water, gave off acetylene and methyl acetylene and was, therefore, a mixture of magnesium allylide and carbide.

Novak[159,160,161] slowly passed acetylene over magnesium heated to temperatures between 400° and 700°. The products obtained, when decomposed by water, yielded acetylene and methylacetylene, showing that two carbides MgC_2, and MgC_3 had been formed. The reaction began at about 400° with the formation of the carbide MgC_2, the yield of which reached a maximum (40 percent of the reaction products) at 490° and then decreased. The forma-

tion of Mg_2C_3 began at 460° and increased regularly with the temperature up to 545°. The amount of carbon formed above 500° was always large. The products obtained between 465° and 515° were hard, compact masses, steel-gray in color, and were decomposed by water only slowly; those obtained above 550° were gray, brittle, and with water decomposed rapidly.

N. V. Electrozuurstof-en-Waterstoffabriek[157] add magnesium to metal or oxide catalysts to improve them for use in cuprene manufacture.

Manganese.—Manganese favors acetylene decomposition. In the work of Tiede and Jenisch[199] in which acetylene was passed over massive manganese in a heated tube, carbon separation began at 450° and oil formation at 480°, against 480° and 540°, respectively, without the catalyst. Under their conditions, when passed over manganese at 600° four percent of the hydrocarbon converted was changed into oil, as compared with 17 percent in the blank run. After contact with manganese but 8.7 percent of the hydrocarbon passed was recovered unchanged against 97.5 percent in a run with no catalyst.

Mercury.—On conducting acetylene through boiling mercury, Hilpert[88] observed small quantities of carbon, but no tar. The formation of traces of mercury alkyls was suspected. Deposition of carbon occurred when Durand[55] exposed acetylene to a temperature of about 500° in the presence of mercury vapor.

Erdmann and Köthner[59] reported that mercury was scarcely acted upon when heated to its boiling point in acetylene.

Palladium.—While no changes took place when Zelinsky and Kasansky[213] conducted acetylene over palladinized asbestos at ordinary temperatures, at 330° the heating tube filled rapidly with carbon. A small quantity of condensate formed, which contained unsaturated hydrocarbons, and blackened and resinified in air.

When Durand[55] conducted acetylene over finely divided palladium heated to about 500°, his only observation was the deposition of carbon on the metal.

When Campbell[41] passed the pure dry acetylene over palladinized copper oxide (one percent palladium), moisture was noticed at 225°-230° and at 300° the tube was choked by a heavy black deposit. No carbon dioxide was formed.

Potassium.—Berthelot[10] observed that when heated gently in acetylene, potassium caught fire and burned, sometimes explosively. An acetylide of potassium was formed, hydrogen was evolved and carbon deposited. Moissan[150] found that at ordinary temperature and pressure potassium had no action on acetylene beyond the formation of potassium acetylide.

Rubidium.—Erdmann and Köthner[59] found that at low temperature, in the presence of acetylene, rubidium became yellow, turning to brown, then took on a dark red glow, and finally became black and brittle. There was copious separation of carbon but no other product was identified.

Sodium.—At low temperatures the only action of sodium on acetylene is the formation of sodium acetylide or sodium carbide.[136] At higher temperatures carbon deposits. When de Forcrand[52] passed a slow current of dry

acetylene over sodium in a small iron boat in a glass tube heated to dull redness, the product was 62.13 percent sodium carbide and 37.87 percent carbon. Perhaps the carbon found was formed by decomposition of sodium acetylide, as Moissan[150] found that when sodium acetylide was slowly heated in a tube of Bohemian glass, acetylene was evolved, a small quantity of liquid hydrocarbons formed, and sodium carbide deposited in the tube. When the heating was carried nearly to the melting point of the glass, the sodium carbide decomposed into carbon and sodium.

Sodium acetylide, hydrogen, and carbon were formed rapidly when Tiede and Jenisch[199] conducted acetylene over heated sodium.

Tin.—While no investigators have reported the use of tin alone, Bahr[3] found that tinned iron markedly repressed carbon formation and aided the conversion of acetylene to liquid products, until at about 475° the heat removed the tin coating. He employed tin-nickel alloys as well. Fischer, Schrader and Ehrhardt[67] also used a tinned iron tube. Fujio[73] passed acetylene through a tinned tube and reported that the tinning aided decomposition.

Uranium.—Durand[55] reported that when acetylene was heated to about 500° in the presence of finely divided uranium, carbon deposited on the metal, but there was no evidence of acetylide formation.

Zinc.—Erdmann and Köthner[59] found that a zinc surface was merely blackened when heated in acetylene to the decomposition temperature of the hydrocarbon. There was no evidence of the formation of an acetylide.

Carbon and a little tar (apparently containing no benzene) formed when Hilpert[88] passed acetylene into molten zinc. Hodgkinson[89] found zinc to have no significant action when it was heated to its melting point (419°) in a stream of acetylene.

Tiede and Jenisch[199] made comparisons between results of passing acetylene for a period of three hours through an empty tube at 600°, and results when gas was passed at the same rate and temperature through the tube containing a porcelain boat filled with a metal.

Of the many metals tried the following changed the course of the reaction:

Lithium	Nickel
Sodium	Copper
Iron	Manganese
Potassium	Finely divided
	palladium and platinum

With the following metals the results of parallel runs with and without the contact agent were alike within experimental error.

Aluminum	Mercury
Antimony	Platinum and palladium
Bismuth	in massive form
Boron	Silver
Cadmium	Silicon
Calcium	Tantalum
Chromium	Thallium
Gold	Tin
Lead	Titanium
Magnesium	Tungsten
Molybdenum	Uranium
	Zinc
	Zirconium

iii.   Combinations of Metals

When a mixture of acetylene (9 percent) and hydrogen was passed over an iron-copper-alkali-catalyst in a hard-glass tube at 250°, Fischer, Peters, and Koch[66] found that 40 to 70 percent of the acetylene was converted into oil. As the catalyst was not readily poisoned, a high degree of purity in the gas mixture was unnecessary.   When the ratio of copper to iron in the catalyst exceeded 1 : 10, the tube quickly became stopped by a deposit of cuprene, but with a 10 Fe:1 Cu catalyst the tube was operable for 10 days.   The addition of nickel to produce a catalyst 10 Fe:1 Cu:1 Ni diminished the formation of cuprene still more and gave a yield of 50 to 55 percent of liquid product, containing 75 percent benzene and 25 percent of heavier oil.

At the same temperature an iron-nickel catalyst (10 Fe:1 Ni) caused a 60 percent conversion into liquid, two-thirds of which was benzene.

With the catalyst 2 Fe:1 Ni at 250°, 30 to 35 percent of the acetylene passed was converted into liquid containing from 85 to 90 percent benzene.   Hydrogenation taking place at the same time produced considerable ethane (9 percent of the gaseous products) and smaller amounts of ethylene and higher unsaturated hydrocarbons.

In the presence of the catalyst 10 Cr:1 Ni about 30 percent of liquid products were obtained at 250°.   In these experiments variation of the temperature over a range of 100° and fluctuation in the rate of passage of the gas from 2 to 12 liters per hour did not affect the yield or quality of the oils. The products consisted of a heavy oil, free from paraffin wax, which collected in the receiver, and a light oil, 90 percent boiling between 50° and 150°, which was absorbed by activated charcoal.   The light oil contained 60 percent of unsaturated hydrocarbons.   One cubic meter of coke-oven gas (which contained acetylene) yielded 85 grams of liquid, of which 75 percent was light oil.

Fischer and Peters[65] studied the hydrogenation and polymerization of acetylene in the presence of catalysts suspended in a heavy oil to compare the results given by catalysts used alone and catalysts suspended in liquid.   Use of

the catalyst in oil suspension had the advantage, particularly in an exothermic reaction, of allowing accurate temperature control and ready dispersal of heat produced. In this work the catalyst was mixed with paraffin oil or methyl naphthalene, and fine bubbles of a mixture of acetylene and hydrogen passed upward through the mixture. The oil was treated with hydrogen in the presence of nickel before use in the acetylene runs.

The progress of the reaction was determined by noting the decrease in the volume of the gas. With a nickel or copper catalyst precipitated on kieselguhr, reaction was evident at 60°, and contraction a maximum at 170°-230°. At temperatures from 100° to 300°, the highest used, all the acetylene was converted. Comparison of results with a nickel-iron-thorium catalyst "dry," and suspended in oil, indicated a greater dependence of reaction rate upon temperature in the liquid studies. With pure nickel, hydrogenation was noticeable even at room temperature. At first only ethane and ethylene were produced, but at 250° the products were ethylene 24.5%, ethane 46.8%, oil, composed of about one-third unsaturates, 22%, "benzine" 6%. When this catalyst was used alone at the same temperature, more polymerization occurred than when the liquid was present. A copper catalyst produced some cuprene as well as the products mentioned.

For large yields of higher hydrocarbons, a mixed catalyst was used. A nickel-iron preparation with the metals in the proportion 1:9 gave at 200°, in a 1:2 mixture of acetylene and hydrogen, 17.4% conversion of the acetylene to ethylene, 5.1% to ethane, 74.3% to liquid hydrocarbons. This is a higher yield, and the product was lighter than that produced by the same catalyst used "dry."

With a copper catalyst, reaction began at 100° and maximum contraction occurred at 230°. Much of the acetylene went to ethylene, some to ethylene and "cuprene tar." No propane, propylene, or higher hydrocarbons were formed over copper alone, although some of these products were always produced when using a mixed catalyst containing copper, iron, and nickel.

By passing acetylene over an alloy containing equal percentages of nickel and tin in the form of fine shavings, Bahr[3] obtained at 280° a condensate with the distinct odor of benzene, at first transparent but soon colored a greenish brown. At about 430° separation of carbon began, and quickly stopped the tube for a distance of 3 to 4 cm. from the entrance of the gas. On lowering the temperature to 380° the carbon separation stopped. With an alloy of 75 percent tin and 25 percent nickel, carbon separation was not quite as profuse, but the reaction was otherwise little different.

When tinned iron turnings were used as contact material a clear condensate appeared in small quantities from 250° and did not take on a brown color even with considerable increase in temperature. As long as the turnings retained the tinned surface there was little evidence of carbon separation. At high temperatures the tin flowed from the turnings leaving the iron surfaces free. At 475° to 480° separation of carbon was observed at a number of points on the catalyst.

Fischer, Schrader and Ehrhardt[67] reported that on passing a mixture of acetylene and hydrogen (in the volume ratio 1:3) through a tinned iron tube at 675° to 700° about 8 percent of the acetylene was converted into benzene. Considerable carbon separated in the heating tube. Decomposition was also studied in the presence of a tin-iron alloy.

Tiede and Jenisch[199] found that alloys of copper with gold, copper with zinc, and copper with aluminum were inactive, while an alloy of copper with nickel aided the decomposition of acetylene. Hilpert[88] passed acetylene over brass turnings without noting any catalytic effect.

Pictet[163,164,165] claimed carbon and hydrogen formation from acetylene or a mixture of acetylene with other hydrocarbons, by their passage through a steel, iron, or porcelain tube, the front part of which was heated to about 500° and the remainder cooled to absorb the heat produced by the dissociation.

Prudhomme[168] outlined a process for manufacturing liquid fuel having the general properties of petrols and benzols, which consisted in adding gases rich in acetylenic hydrocarbons to water gas or producer gas and passing the mixture over a hydrogenation catalyst, then over a dehydrogenation catalyst, and finally over pumice impregnated with nickel and cobalt to effect polymerization of the acetylene hydrocarbons.

Cyclic hydrocarbons, particularly those of a hydroaromatic nature, are prepared by I. G. Farbenindustrie[96] by passing acetylene alone, or in mixtures, over heated condensation catalysts, such as compounds of arsenic or of metals, except arsenic, having a specific gravity of 4.4 and belonging to the second to seventh groups. The products of this step are passed with hydrogen over metallic hydrogenating catalysts. The condensation is effected at 250°-300° and the subsequent hydrogenation at 150°-250°.

I. G. Farbenindustrie[97] thermally decomposes acetylene or other unsaturated hydrocarbons at temperatures below 500°, the upper temperature limit being selected so that 90 percent of less conversion to carbon black occurs. The remainder of the acetylene is converted into saturated hydrocarbons. Cobalt, iron or nickel may be used as catalysts, with such activators as compounds of chromium or of the alkali metals.

iv. Other Substances

Ferric Oxide.—Gooch and Baldwin[76] found that ferric oxide heated in acetylene at temperatures varying from 150° to 360° glowed and became covered with a dark carbonaceous deposit. The iron content of this deposit varied from 2.80 to 5.86 percent.

Silver Oxide.—Gooch and Baldwin[76] found that acetylene acts upon silver oxide at ordinary temperature, giving silver, perhaps resulting from decomposition of an acetylide first formed. The reaction is usually explosive.

Other Oxides.—Berl and Hofmann[8] reported that the oxides which they studied—stannic oxide, calcium oxide, and silicon dioxide—were unfavorable to acetylene polymerization, and turned the reaction toward formation of methane, hydrogen, and carbon.

Ceric Sulphate.—The Compagnie Générale de Produits de Synthèse[47] claimed that hydrocarbon gases containing acetylene and methane coming from a gas producer were polymerized by heating to about 80° in the presence of a catalyst containing ceric sulphate.

Ferric Nitride.—Hodgkinson[89] reported that ferrous nitride when heated in acetylene became highly carburized. Ammonia was also formed.

Ferrous Sulphide.—To avoid carbon deposition during polymerization Bahr[3] heated acetylene in the presence of ferrous sulphide. He used this substance because sulphur compounds had been found effective in checking the decomposition of carbon monoxide to carbon and carbon dioxide. When the acetylene was passed over the ferrous sulphide in a glass tube, the first drop of condensate, of pale yellow color, appeared at 300°. Soon a mobile dark brown tar flowed along the tube. No carbon separation was noticeable and the catalyst retained its metallic luster. Visible separation of carbon occurred above 430°, accompanied by rapid formation of tar fog. Reduction of the temperature to 350° did not stop the separation of carbon on the contact material. Dilution of the acetylene with 50 percent of methane made no noticeable change in the reaction.

It was suggested that failure of the ferrous sulphide to stop carbon formation entirely was due to slow conversion of the contact layers into metallic iron. Iron decomposes acetylene from 300° upwards with separation of carbon. Fujio[73] also used a metal tube coated with iron sulphide and claimed that it aided decomposition and increased the proportion of low-boiling constituents in the tar.

Nickel Carbonyl.—Binnie[29] found that nickel carbonyl, added either as such or made during the process by contact of added carbon monoxide with the nickeled tube, gave yields of oil up to 65 percent when a mixture of acetylene, hydrogen and nitrogen was heated with it at 190°. The oil was low boiling and appeared to contain a large proportion of olefins.

Phosphoric Acid.—Bahr[3] passed acetylene through pumice impregnated with concentrated phosphoric acid. The first separation of carbon was detected at 470° to 480°.

Sodium and Potassium Hydroxides.—Some decomposition of acetylene to carbon and hydrogen took place when Fry, Schulze and Weitkamp[72] passed the gas through a fused mixture of equimolar weights of sodium and potassium hydroxides maintained at 300° to 325°. Methane, and sodium and potassium orthocarbonates were also produced.

Stannous Chloride.—Acetylene passed over pumice which had been impregnated with stannous chloride and heated in hydrogen at 500° showed little change beyond slight separation of carbon.[3] When acetylene with ammonia was passed into the tube filled with stannous chloride-pumice at 400°, as soon as the mixture reached the contact material, flame struck backward in the gas stream and then went out, with dense separation of carbon. The pumice became covered with ammonium chloride and there was a slight formation of tar with a pyridine-like odor.

3. In Admixture with Other Gases

The dilution of acetylene has been found to affect both the speed of reaction and the nature of the products obtained. Some pyrolyses of diluted acetylene have already been taken up. Others are discussed below, particularly those in which a high proportion of diluent is used.

Berthelot[11] found that acetylene mixed with an equal volume of nitrogen, carbon dioxide, methane, or ethane decomposed a little more slowly than the undiluted gas.

Catalysis of acetylene mixed with methane or hydrogen (10 percent acetylene to 90 percent of diluent) was studied by Fischer, Bangert, and Pichler.[64] They found that in this mixture active carbon, silica gel, and to some extent pumice catalyzed the acetylene polymerization, but mica, graphite rods, and barium chloride, or active carbon or silica gel treated with alkali or metallized, produced practically no change at 600° and caused heavy carbon deposition above this temperature. In order to obtain oil from the dilute acetylene in an unpacked tube, a temperature between 680° and 730° was necessary, which was higher than that required with acetylene alone. In a long run, at 660° to 680°, the oil formation reached 40 percent of the acetylene treated. When after 30 days the oil yield began to drop, it was restored by increasing the temperature to 700°-720°. It was then possible to continue the run for 55 days.

Fujio[73] noted that hydrogen, methane, carbon monoxide and carbon dioxide had a marked effect upon the chemical nature of the tar produced by acetylene pyrolysis. Their presence caused reaction to go on more smoothly. Carbon dioxide caused the appearance of a greater percentage of light oils in the product. Fujio also noted, as had others, that the carbon deposited on the catalyst by decomposition of acetylene seemed to play an important rôle.

Binnie[29] pyrolyzed mixtures containing small percentages of acetylene with hydrogen and nitrogen. A mixture of 4 percent acetylene and 96 percent hydrogen passed through a silica tube at 600° produced ethylene and methane. Charcoal or silica gel were not effective catalysts, while copper, iron-nickel, or cobalt precipitated on silica gel were very reactive, and transformed acetylene at little above room temperatures. Reduction of the hydrogen content of the mixture to 20 percent by addition of nitrogen decreased hydrogenation and increased the formation of oil, which reached a maximum of 40 percent of the acetylene used. A nickel catalyst produced ethane but no oil.

Addition of nickel carbonyl in carbon monoxide, or passage of the mixture of acetylene, nitrogen, hydrogen and carbon monoxide through a metal tube coated with nickel, gave increased yields of oil, reaching 65 percent of the acetylene at 190°. The oil boiled to 85° and was apparently olefinic, as it reacted violently with sulfuric acid and bromine. Oil formed in the presence of iron or sulfur was higher boiling.

Patents.—The I. G. Farbenindustrie A. G.[95] reports that an oil was obtained by passing a mixture of acetylene and ethylene at 525°-550° through an externally heated aluminum tube within which silicon was deposited on a plate. An oil of lower boiling point was produced by passing a mixture of acetylene, ethylene, and nitrogen through a vessel coated internally with tin

and then with powdered silicon. A condensate containing 13 percent of butadiene was obtained by passing a mixture of acetylene and ethylene through a manganese-copper tube coated internally with tin, while benzene was said to be formed when using a manganese, copper or brass tube coated internally with zinc.

In further patents, the I. G. Farbenindustrie A.-G.[98,100] claims that valuable hydrocarbons such as benzene and butadiene may be obtained from reaction of olefins such as ethylene with acetylene at a high temperature, under such conditions that the hydrocarbons come in contact with elements of the fourth group of the periodic system such as tin, silicon, lead, carbon in the form of graphite, or with zinc or aluminum or alloys having a high content of these elements.

According to Lichtenhahn[119] addition of 5-15 percent of nitrogen to acetylene prior to treatment by the action of heat and catalysts restricted or prevented the coking or discoloration of the condensation products. It was claimed that coke losses were reduced to less than 6 per cent.

N. V. de Bataafsche Petroleum Maatschappij[156] forms oily liquids, boiling from 60°-320°, by heating acetylene to about 440° in the presence of a catalyst such as finely divided iron or magnesium bromide, in an inert liquid medium such as liquid paraffin, transformer oil, or a hydronaphthalene. Ethylene may be added to the acetylene before subjection to this process.

C. *Action of Chemical Reagents.*

Cuprous Chloride.—Nieuwland, Calcott, Downing, and Carter[158] have accomplished the controlled polymerization of acetylene at ordinary temperature by passing it into a cuprous chloride solution containing ammonium chloride to increase the solubility of the copper salt. They isolated vinylacetylene, divinylacetylene and a tetramer of acetylene believed to be 1, 5, 7-octatriene-3-ine.

The first step in this reaction, these workers believe, is formation of a complex cuprous salt which is in equilibrium with normal acetylene and activated acetylene. An activated acetylene molecule then reacts with a molecule of normal acetylene to produce vinylacetylene:

$$HC\equiv CH + =C=CH_2 \longrightarrow HC\equiv C-CH_2=CH_2$$
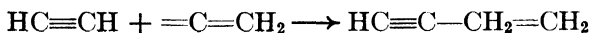
By reaction with an activated acetylene, vinyl acetylene may then produce divinylacetylene, or a vinylacetylene molecule may become activated and by reaction with a like molecule produce the tetramer. The relatively low yield of tetramer shows this second reaction to be much slower than the vinylacetylene-acetylene reaction. There is also the possibility of an active vinylacetylene molecule reacting with acetylene to form the compound: $H_2C=CH-CH=CH-C\equiv CH$ which might itself double to a compound $C_{12}H_{12}$. The existence of these last two substances is indicated but has not been proved.

Vinylacetylene is a colorless liquid boiling at 5°. On heating under pressure, it readily polymerizes, with or without polymerizing agents, to form

viscous drying oils and finally hard resinous solids. These polymers contain acetylenic hydrogen.

Divinylacetylene is also a colorless liquid, of alliaceous odor, boiling at 83.5°. It readily absorbs oxygen to form an explosive peroxide, and is itself extremely dangerous to handle, as on standing it turns into explosive gels and resin. It decomposes thermally at 105°-110°, but when heated at lower temperatures in an inert atmosphere forms by polymerization a viscous liquid and hard brittle resin. Intermediate in this polymerization are liquids which are drying oils, and are converted by oxidation and polymerization into films which are softened by no solvent and resist all but the most vigorous oxidizing agents. The development of explosive products in the liquid may be prevented by antioxidants.

The C_8H_8 "tetramer" is a colorless liquid chemically similar to divinylacetylene, which polymerizes on gentle heating, and has an apparent boiling point of 156°, with violent decomposition.

A patent of Collins[46] covers the polymerization of divinylacetylene and this tetramer to drying oils. Temperatures of 80° to 100° are used, the degree of polymerization attained depending upon the time and temperature of treatment. In examples, it is stated that four hours refluxing of divinylacetylene in the presence of air (85°-90°) produces a 12-18 percent yield of a viscous polymer having the general properties of a bodied drying oil. The acetylene tetramer is quantitatively converted into a drying oil by heating for three hours at 100°. These substances can also be polymerized in mixture, and in the presence of cobalt driers and of solvents.

Aluminum Chloride.—Baud[5] reported that dry acetylene was rapidly absorbed by anhydrous aluminum chloride in the cold, and at an increased rate of 70°. When it was passed over the salt at 70° to 130°, in part it formed a black sublimate with the empirical composition 7 $(C_{10}H_{15.6})$, $2Al_2Cl_6$. When this was distilled with quick-lime, three hydrocarbon fractions were obtained with the following boiling ranges and empirical formulas: 150°-190°, between $C_{10}H_{18}$ and $C_{10}H_{16}$; 190°-260°, $C_{10}H_{16}$; 260°-300°, $C_{10}H_{14}$. The greater portion of the acetylene and aluminum chloride formed a non-volatile, black substance easily taking up oxygen, with empirical formula 7 $(C_{20}H_{15})$, Al_2Cl_6. On distillation with quicklime this substance yielded a small hydrocarbon fraction corresponding in composition to the formula $C_{15}H_{20}$, boiling from 150°-350°. The higher boiling portions of the distillate were nearly solid and contained anthracene.

D. *The Explosive Decomposition of Acetylene including Detonation and Action of Electric Sparks.*

Acetylene is decomposed to its elements by proper excitation. If a wire is heated in an atmosphere of acetylene, for example, a charge of some detonator, as mercury fulminate, exploded in it, or a spark passed, decomposition will ensue, which may be local, confined to the immediate vicinity of the exciting agency, or may produce a flame wave which will spread with greater or less rapidity throughout the mass of the hydrocarbon. Conditions of

temperature and pressure and the rapidity with which heat is dissipated determine whether the breakdown of acetylene is restricted to a small zone, whether it becomes a flame, or a decomposition of explosive violence. At atmospheric pressure, for example, explosion of acetylene is not produced by sparks, but when the gas is under slightly increased pressure, sparking may bring about violent detonation. It is obvious that exact knowledge of acetylene decomposition, and of the conditions under which explosion is possible, are essential to its safe handling and utilization. Because of the widespread commercial use of acetylene, its explosive properties have been extensively investigated.

Berthelot[9] was the first to report that acetylene was decomposed by electric sparks with deposition of carbon.

de Wilde[53] also decomposed acetylene by passage of induction sparks between platinum points.

Maquenne[134] found that acetylene decomposed only partially when o.1 to 0.2 gram of mercuric fulminate was exploded at the center of a liter flask filled with the gas. The residual gas contained more than 90 percent of acetylene. Decomposition was accompanied by formation of a small cloud of lampblack, and was limited to the gas in the sphere of action of the fulminate. With one gram of the fulminate exploded at the end of long lead tubes filled with acetylene the explosive wave traveled through a distance of 5 to 8 meters, depending upon the diameter of the tubes, decomposing the gas to carbon and hydrogen.

Further work by Berthelot and Vieille[25] confirmed the finding that when acetylene under ordinary pressure was subjected to the action of an electric spark, a red-hot platinum or iron wire, or a charge of fulminate, decomposition did not extend far. When the gas was under a total pressure exceeding two atmospheres, however, the gas acted much as does an explosive mixture. If decomposition was produced at any point it spread rapidly through the entire volume of the gas, which decomposed into hydrogen and bulky pulverulent carbon. Under an initial pressure of 21 kg. per sq. cm., the pressure developed by the decomposition was 210 kg. per sq. cm., and the change was complete in 0.018 second.

Liquefied acetylene was also readily decomposed, though relatively slowly when the change was initiated by simple ignition. When a bomb containing both liquid and gas was set off there was a change in the curve of pressure which indicated two distinct phases of the explosion, one probably corresponding to the decomposition of the gaseous part, and the other, which lasted longer and raised the pressure much higher, to the decomposition of the liquid. With 18 grams of the liquid in a steel bomb of 48.96 cc. capacity, the final pressure was 5,564 kg. per sq. cm.

Shock caused by fall of the steel bomb from a height of 6 meters did not cause the explosion of either compressed or liquefied acetylene. If the bomb broke there was no explosion of the gas compressed to 10 atmospheres, but if the vessel contained liquid acetylene, the fracture was followed after a short time by an explosion. When liquid acetylene was decomposed by a small

quantity of fulminate, violent detonation took place and the fragments of the bomb were covered with carbon liberated from the gas.

The publication of this work attracted much notice and was widely quoted.[44,100]

Berthelot and Vieille[27] showed that an intermediate pressure zone, between normal pressure, when explosion does not occur, and a total pressure of two atmospheres where explosion is almost certain, the production of an explosion depended on the means of excitation used and the amount of cooling of the system. They brought about decomposition in this intermediate zone in vessels and tubes of various sizes, thus varying the amount of cooling, and using for initiating reaction an incandescent metal filament or a charge of fulminate. Explosion was produced in glass vessels by ignition at an excess pressure of 52 cm. of mercury, and at 17 cm. of mercury by detonation. In a long metal tube, there was no propagation of the decomposition even when an excess pressure of one atmosphere was used, regardless of whether the excitation was produced by a charge of fulminate or a hot wire.

Bone and Cain[30] and Bone and Jerdan[33] reported that rapid decomposition of acetylene and deposition of carbon occurred when an arc between carbon electrodes acted upon the gas. The gaseous product was hydrogen with a few percent of methane, and the presence of a minute quantity of naphthalene was said to be apparent from the odor.

Gerdes[75] early discussed the decomposition of acetylene with reference to the hazard involved in using this gas to light railroad coaches. He reported that sufficient local overheating might occur when a small amount of water was added to a large amount of carbide—bringing the entire mass to glowing— to exceed the temperature of acetylene decomposition. It was found at the Pintsch works that heating a cylinder containing acetylene compressed to 6 atmospheres, or heating a tube leading to such a cylinder caused violent explosion. Mixtures of acetylene and oil gas decomposed less readily than the pure hydrocarbon, and such a mixture containing 30 percent acetylene was considered safe to use. Addition of 50 percent hydrogen to acetylene made it much less dangerous.

Körting[114] also found that mixtures of oil gas and acetylene were less subject to explosive decomposition than acetylene alone.

Berthelot and Vieille[28] studied mixtures of acetylene with hydrogen and city gas, and found that a decomposition initiated by a hot wire in a 50:50 mixture of acetylene and hydrogen proceeded only a limited distance even at a pressure of 4 atmospheres, while in a 1:3 mixture a pressure of 10 atmospheres was safe. The limits were somewhat lower in small vessels. Higher limits were found in city gas and acetylene mixtures, on account of the absorption of heat by carbon monoxide at high temperature.

Lewes[118] found that contact of water with a large amount of carbide in an acetylene generator could produce a temperature of 804°. A temperature of 780°, he stated, was sufficient to cause complete decomposition of acetylene, while below this polymerization began, producing benzene, styrene, anthracene, naphthalene, as well as ethylene and methane.

Berthelot and Vieille[26] also investigated the explosive properties of acetone solutions of acetylene. Explosion of a fulminate charge in the gas space of a cylinder containing a 41.25 percent solution of acetylene in acetone under pressure of 13 kg/cm² caused no change in the solution. This may be contrasted with the behavior of liquid acetylene, which shattered the steel flask on similar treatment. However a 64 percent acetylene solution under 20 kg/cm² pressure exploded.

The decomposition of the solution, they noted, was slow, requiring 0.4 second, as compared with .00004 second for the explosion of a mixture of hydrogen and oxygen. It was also much slower than the combustion of acetylene. The acetone of the solution was decomposed during the explosion.

Vogel[200] summarized the available information on acetylene decomposition. Liquid acetylene is exploded by a glowing platinum wire or silver fulminate. It explodes even at ordinary pressure, and the explosive force approaches that developed by gun cotton. A sharp shock causes acetylene breakdown only when accompanied by warming or incandescence of a solid substance. This warming may occur during acetylene compression or its passage through a narrow opening. Sharp pressure changes may explode compressed or liquid acetylene.

Janet[104] found that a solution of acetylene even at a pressure above 10 atmospheres—considered by Berthelot and Vieille the safety limit—is safe when it is impregnated in infusorial earth or other porous material.

Claude[45] found that at −80° acetone dissolved 2000 volumes of acetylene at atmospheric pressure, and increased 4 to 5 times in volume. A platinum wire heated electrically to redness could be kept indefinitely in this solution or in liquid acetylene without explosion occurring.

At a conference on the dangers involved in handling acetylene[44] it was reported that acetylene might be passed through a tube at 600°-1,000° without explosion. It was advised that all copper be kept out of contact with compressed acetylene. Pictet was reported to have liquefied acetylene at −80° and to have failed to explode it even by dropping it off cliffs.

Berthelot and Le Chatelier[24] made photographic studies of the velocity of explosion of acetylene detonated by fulminate or chlorate. The acetylene was under pressures of from 6 to 36 kg/cm². The flame was observed in a glass tube, and was found to increase continuously in speed, usually rupturing the tube before a uniform velocity was obtained. Velocities of 1,000 meters per second at 6 kg. and 1,600 meters per second at 30 kg. were observed.

Mixter[145] exploded pure dry acetylene confined in glass tubes under a pressure of 3 atmospheres and heated to temperatures of 325° to 450°, by electric sparks passed between platinum electrodes projecting into the gas. Decomposition was incomplete, as it was also in experiments carried out in a bomb at room temperature. Twenty to 50 percent of acetylene remained in the residual gas. Mixter believed that decomposition was more complete in the experiments of Berthelot and Vieille[25] under pressure varying from 5 to 30 atmospheres.

In further detonation experiments,[146] in which the acetylene was mixed with nitrogen, hydrogen cyanide was produced. As a rule, the amounts of hydrogen cyanide tended to increase as the proportion of nitrogen in the mixture was made larger, but the results were not regular. Ammonia was also detected in some cases, but no cyanogen was found. The relationship between the initial pressure and the amount of acetylene found after explosion was not precisely determined, but the quantity of acetylene increased with pressure up to 4 percent at 3 atmospheres and diminished again at 5 atmospheres.

Using higher pressures of acetylene in a steel bomb immersed in a calorimeter, initiating explosion of the gas by means of electric sparks, Mixter measured the heat of dissociation of acetylene.[147] He found 53,300 calories per gram mole or 2,050 calories per gram. In these experiments at high pressures no measurable quantity of acetylene was found in the gas remaining after an explosion.

A number of cylinders containing liquid acetylene were destroyed in work described by Rasch[170] in a way to afford as much information and satisfy as much curiosity as possible. Against the gas space of one cylinder a large charge of picric acid was exploded, which failed to detonate the liquid below, although the cylinder was ruptured. A smaller charge of picric acid exploded against the lower portion of the cylinder caused violent explosion of the liquid hydrocarbon, which produced a dense cloud of smoke and pulverized the cylinder. A rifle bullet through the gas space caused no explosion, and unfortunately the supply of acetylene ran out before the effect of a bullet through the liquid could be tried.

Frank[71] found that when pure acetylene was exploded under a pressure of five or six atmospheres, the lampblack obtained was contaminated with oily products. The carbon formed was free from oil, however, if the acetylene was mixed before explosion with carbon monoxide or carbon dioxide in the proportions of the equations:

$$C_2H_2 + CO = H_2O, \text{ and}$$

$$2C_2H_2 + CO_2 = 5C + 2H_2O$$
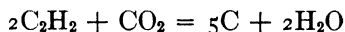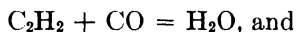
The initial pressure of the acetylene-carbon monoxide mixture was at least six atmospheres. Under these conditions the maximum pressure developed during the explosion was 40 to 50 atmospheres. Because of the high temperature of the explosion (it was stated) the reaction was incomplete and only 85 percent of the theoretical quantity of carbon was obtained. The lampblack formed in this way had a high specific gravity (1.93 to 2.0) and an electrical conductivity much greater than that of any other form of carbon.

Caro[42] contributed a lengthy discussion of the causes of acetylene explosions, in which he summarized prior work in detail and reported a considerable amount of experimentation.

Burrell and Oberfell[40] observed that a "mild" explosion accompanied by the formation of much carbon resulted when acetylene under 5 atmospheres pressure was exposed to a white hot platinum coil. The gas exploded "with

great violence" at a pressure of 3 atmospheres when a small electric spark from an induction coil was used as the source of ignition.

When Fowler and Mardles[68] subjected acetylene to induction sparks between copper electrodes a bright flash occurred in the bulb containing the acetylene and threads of carbon bridged the spark gap.

Alexejew[2] found that when acetylene decomposition was started by a hot wire, the tendency to form a flame wave at constant temperature was favored by increase in pressure, and at constant pressure by increase in temperature. He proposed a relationship $N p^2 + M p\sqrt{T} = 1$ for conditions of propagation of the decomposition, where M and N are constants. This is only approximate, as the amount of cooling which occurs during the decomposition, a vital factor in its spreading, is largely determined by the vessel in which reaction takes place. Thus, in a tube of 3 cm. diameter at 280°-440° Alexejew found that no flame was produced, while in an 8.5 cm. tube violent explosion occurred at 260°. At any given temperature, a small addition of hydrogen, nitrogen, ammonia, or ethylene, raised the pressure necessary for inflammation; a somewhat greater addition reduced the necessary pressure, and large addition caused a new increase in the pressure needed. Slight addition of mercury vapor somewhat lowered the "inflaming pressure," while with more mercury an increase was observed. These results he explained from a kinetic standpoint, the explanation involving the formation of cyanogen when nitrogen was added.

. Rimarski and Konschak[177] found that in contact with heated iron surfaces acetylene decomposed explosively at temperatures above 510°, while below this temperature no explosion occurred. Some contact agents greatly lowered the temperature of decomposition. Copper at 300°-250°, finely divided iron under 180°, finely divided silver gently heated caused acetylene breakdown, and reduced the flashing temperature to 460°-500°. Iron, copper and manganese oxides were able to cause explosive decomposition between 240° and 310°, while active carbon, aluminum oxide, and silicon dioxide had a midposition, producing explosive decomposition at 400°-500°. By adiabatic compression in the presence of iron, acetylene was broken down by a pressure of 27 kg./cm².

Following a disastrous fire in an acetylene manufacturing plant, Rimarski[175] reviewed the literature on the explosive decomposition of acetylene, summarized his own work on this reaction, and outlined the safeguards necessary in handling this hydrocarbon. Some of this work had been previously published from the Physikal-Technischen Reichsanstalt.[173]

He reported that "glowing" carbide—carbide made incandescent by adding a small amount of water to a large amount of carbide—caused explosion of acetylene at 1.6 atmospheres total pressure. A glowing platinum wire caused decomposition of pure, dry acetylene as under the following conditions:

At 10° under a pressure 0.6 atmosphere above atmospheric
    100° " " " 0.33 " " "
    140° " " " 0.10 " " "

If the wire was fused in the gas, decomposition was produced still more readily. Water vapor raised the explosive limits.

The Reichsanstalt work showed that when passing acetylene through a heated tube:

1. At 500° at pressures to 3 kg./cm² no explosive decomposition occurred.

2. At 510°, under 2.05 kg./cm² pressure, and a flow rate of 0.4 liters per minute, explosion first occurred. With increasing temperature and flow rate the pressure necessary for explosion dropped.

3. Extrapolation to zero (quiet gas) gave 1.37 atmospheres at 540°-590° as an explosive limit.

4. A pressure of 170 kg./cm² had to be attained to explode acetylene by adiabatic compression.

When working at initial pressures up to 9 kg./cm², the final explosion pressures were about eleven times the initial. Presence of water or acetone vapor reduced the pressure attained. If a detonation wave occurred, however, the pressure increase might be much greater, even reaching 80 times the initial pressure. Rimarski[174] had reviewed this work briefly in earlier papers.

At about the same time Schläpfer and Brunner[191] investigated the relation of polymerization and thermal decomposition of acetylene to its explosion. They introduced acetylene into small evacuated quartz or Pyrex flasks, at definite temperatures. Decomposition occurred only at temperatures above 500°; polymerization was already apparent at 300° and went on rapidly above 450°. Polymerization released heat and this heat, if not dissipated, could bring the acetylene into the explosive zone. By choice of decomposition conditions, however, polymerization could be practically eliminated. In the technical preparation of carbon by spark decomposition of acetylene, for instance, the gas is heated with extreme rapidity, producing a carbon uncontaminated with tar.

The reaction at 420° was studied kinetically and appeared to be bimolecular. As glass powder produced no change in reaction rate the changes occurring were believed to be homogeneous. Pease,[162] it will be remembered, came to the same conclusions. Fine iron powder catalyzed decomposition of carbon to its elements, an effect intensified by deposition of carbon upon it. If the iron was present in but small amount, decomposition and polymerization went on simultaneously.

Explosive decomposition of acetylene, they stated, might occur by local overheating and spreading of the decomposition to all parts of the gaseous mass, usually as a "puff," but in some cases as a real explosion, or by heating of the entire mass to explosion temperature. In the work of Berthelot and Vieille, and of Rimarski, no regular relationship had been found between temperature of streaming gas and pressure necessary to make explosion possible, so that this spontaneous decomposition of acetylene appeared to be different from the combustion of hydrocarbon mixtures with oxygen. Schläpfer and Brunner found a direct relationship, the pressure needed for explosion dropping as temperature increased. Pressure variation was of greatest moment at high temperatures. They attributed the discrepancy between

their work and Rimarski's to the presence of finely divided carbon in the latter's experiments. Carbon accelerates the decomposition, but does not reduce the pressure necessary to explosion and may increase it. At the surface of the carbon, and of finely divided iron also, rapid decomposition goes on, but the decomposition does not spread into the body of the gas. Finely divided materials have in some other cases been found to check explosions.

Small reaction tubes carry away the heat produced by polymerization more effectively than do large tubes, so that there is less danger of explosion in small tubes. Slow heating produces more polymerization and less decomposition than rapid heating. Under 0.6 atmosphere pressure above normal they found explosion at 700°, a lower pressure than reported by Rimarski, who apparently heated his gases more slowly. Below 500° these workers concluded that there was no danger of explosion under the pressures technically used in acetylene preparation.

The action of iron oxides on these reactions is complex. Magnetic oxide appears first to catalyze a polymerization at 530°, a temperature at which the oxygen of ferric oxide apparently forms carbon dioxide. The oxides appeared in some cases to check decomposition, and in no case to lower the explosive limit, although Rimarski and Konschak claimed that metal oxides such as those of iron and copper might lower the flashing temperature several hundred degrees. This lowering, in the earlier work, Schläpfer and Brunner attributed to local overheating, as Rimarski and Konschak had found that there was active reaction at the oxide surface.

Impurities which might be present in commercial acetylene, such as water vapor, phosphines, silicanes, or ammonia, appeared not to influence the decomposition. Oxygen alone reduced the explosive temperature, probably through increased temperature and pressure caused by combustion. The minimum pressures found for spontaneous decomposition of acetylene were as follows:

$$550° - 2.5 \text{ atmospheres}$$
$$600° - 1.5 \quad ''$$
$$700° - 0.6 \quad ''$$

Morani[152] produced pigment carbon by explosion under pressure of a mixture of acetylene and air, mixed with an exothermic gas as methane, ethane, or illuminating gas.

E. *Action of Electric Discharge.*

In contrast with the disruptive effects of the electric spark, the silent electric discharge converts acetylene into polymers. Low-boiling polymers may be obtained by careful control of conditions, but if reaction proceeds without regulation, the product is usually a brown resin, somewhat explosive, and avidly absorbing oxygen if brought in contact with air.

By means of high-frequency discharge, with the electrodes kept at −60°, Mignonac and de Saint-Aunay[144] obtained from acetylene a 70 percent yield of a colorless liquid whose molecular weight indicated it to be a trimer of acetylene. It slowly underwent further polymerization. It was not, however,

a pure compound. Formation of metal derivatives showed it to contain 40% of diacetylenes, and no monoacetylenes. Oxidation with potassium permanganate or ozone converted it into formic, oxalic, propionic, and succinic acids; hydrolysis of the ozonide gave formaldehyde and reduction of the trimer in the presence of platinum produced hexane. These reactions were taken to indicate that the trimer was a mixture of dipropargyl, $HC\!:\!C\cdot CH_2\cdot CH_2\cdot C\!:$ CH; methylpentadiine, $HC\!:\!C\cdot CHMeC\!:\!CH$; and divinyl acetylene $H_2C\!:$ $CH\cdot C\!:\!C\cdot CH\!:\!CH_2$.

The reaction was thought to take place through activation of acetylene molecules, each of which then added as $H—$ and $—C{\equiv}CH$ to the triple bond of an ordinary acetylene molecule to form vinylacetylene, or to vinylacetylene to form dispropargyl or methylpentadiine. It was further suggested that vinylacetylene might become activated and add as $CH_2\!:\!CH\cdot C\!:\!C\cdot$ and $\cdot H$ to a neutral acetylene molecule to produce divinyl acetylene. This mechanism of polymerization is outlined by the following equations:

$$(1)\quad HC{\equiv}CH$$
$$\uparrow\ \ \uparrow \longrightarrow CH_2{=}CH{-}CH{\equiv} \longrightarrow HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$$
$$HC{\equiv}C\ \ H \qquad \text{Vinylacetylene} \qquad\qquad \text{Dipropargyl}$$
$$\uparrow\ \ \uparrow$$
$$HC{\equiv}C\ \ \ H$$

$$(2)\quad CH_2{=}CH{-}CH{\equiv}CH \qquad HC{\equiv}C{-}CH{-}C{\equiv}CH$$
$$\uparrow\ \ \ \uparrow \qquad \longrightarrow \qquad\qquad CH_3$$
$$H\quad\ C{\equiv}CH \qquad\qquad \text{Methylpentadiine}$$

$$(3)\qquad\qquad HC{\equiv}CH$$
$$\nearrow\quad\searrow$$
$$CH_2{=}CH{-}C{\equiv}\ \cdot H \longrightarrow CH_2CH^-C{\equiv}C{-}CH{=}CH_2\ \text{Divinylacetylene}$$
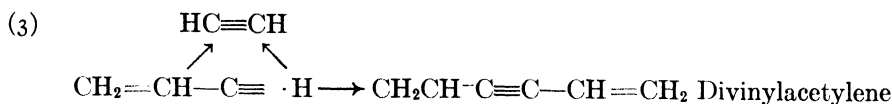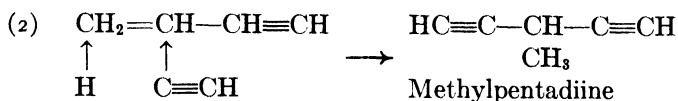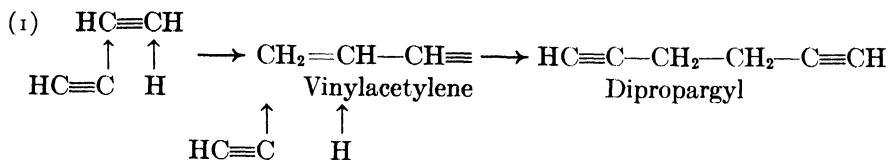
In the work of other investigators, which will be taken up in approximately chronological order, no such temperature control was used and polymerization went much farther, yielding heavy liquids or solids.

de Wilde[54] reported that the silent electric discharge acting on acetylene produced a yellow oily liquid which solidified after a few hours to a brown amorphous substance.

A. Thénard[197] observed that acetylene exposed to the action of the silent electrical discharge was condensed to liquid and solid products having the same empirical formula as acetylene.

Berthelot[15,16,17] found that the silent discharge converted acetylene into a thick, brown liquid, a brown solid polymer, and a small amount of gas. The gases consisted of 92 percent hydrogen, 4 percent ethane, and 4 percent ethylene. Heated in an atmosphere of nitrogen, the solid polymer decomposed with evolution of heat, and produced a small quantity of styrene, slightly volatile tarry hydrocarbon material, a carbonaceous residue and a small amount of gas.

Schützenberger[195] found that acetylene, sealed in glass bulbs and subjected to the silent electrical discharge, condensed to a resinous solid. Evidently air was present, as the product contained oxygen.

By subjecting acetylene to high-frequency discharge, Jackson and Northall-Laurie[103] also obtained a semi-solid brown substance which set to a hard insoluble solid on exposure to air. If care was taken to avoid secondary reactions caused by too prolonged action of the discharge the solid was, by analysis, a polymer of acetylene. It absorbed oxygen readily up to about 8%. When heated out of contact with air, an oil distilled off and small amounts of methane and hydrogen were evolved.

Losanitsch[130] found that the silent electrical discharge converted acetylene into a thick brown liquid which later changed into a solid mass. This mass consisted of two parts—one which was soluble in an alcohol-ether mixture and after evaporation of the solvents remained as a viscous, fragrant mass; the other, present in larger quantity, a tarry-odored solid insoluble in all solvents tried. Under similar conditions Jovitschitsch[105] obtained an extremely insoluble condensation product which he reported possessed strong "radioactive" properties. Because of inconsistencies in his analysis—carbon plus hydrogen not totalling 100 percent—he claimed the transformation of elements by the electrical discharge.

Losanitsch[131] found, as had others, that the condensation product obtained from acetylene by action of the electrical discharge absorbed oxygen rapidly on exposure to air. During the oxygen absorption, iodine was liberated from potassium iodide and a photographic plate was acted upon, but these changes stopped as soon as the oxygen absorption ended. Losanitsch stated, therefore, that the "radio-activity" of Jovitschitsch was undoubtedly produced by very small quantities of ozone. Later Losanitsch[132] reported that acetylene was not only polymerized, but also decomposed into carbon and hydrogen by the electrical discharge *in vacuo*. The carbon produced remained mixed with the polymerized product, while the hydrogen united with acetylene to form a soft soluble mass.

Jovitschitsch[106] again could not make the carbon and hydrogen figures on the electrical condensation products of acetylene reach 100 percent, and, as before, Losanitsch[133] attributed this result to absorption of oxygen by the polymerized product, which later analysis by Jovitschitsch[107] confirmed.

By subjecting acetylene to the action of the silent discharge while the gas passed through the annular space between two concentric glass tubes, Kaufmann[108] obtained, when the reaction vessel was allowed to become warm, a mixture of solid and liquid. If the vessel was kept cold, a liquid was the only product. This liquid was a brown viscous oil, polymeric with acetylene and unstable, which changed on warming, on being kept in solution, or by the attack of almost any chemical agent, into a solid that appeared to be identical with the product described by de Wilde.[54] The liquid decomposed and carbonized above 100°, but a small quantity distilled at 70° under 10 mm. pressure. The residue in the flask after distillation changed to a plastic mass which eventually became brittle. The solid product which formed in the warm re-

action vessel was obtained more conveniently by warming a solution of the liquid product in ether at about 60°. It was a pale yellow, odorless powder which was insoluble in all solvents.

Both the liquid and the solid rapidly absorbed oxygen and during such absorption they produced an action on a photographic plate, this result confirming the earlier work of Losanitsch.[131] Although not acted upon by a dilute solution of bromine the solid was attacked by bromine in concentrated solution, and hydrogen bromide was evolved. The liquid absorbed bromine, producing a pale yellow powder with the empirical composition $(C_2H_2Br)_{28}$. A solution of the liquid in carbon tetrachloride, on treatment with alcoholic silver nitrate, yielded a pale yellow precipitate of a silver derivative, which exploded on heating. This indicated the presence of the acetylenic hydrogen. By oxidation with alkaline potassium permanganate the liquid product yielded benzoic, isophthalic, and terephthalic acids, which were also obtained, although with greater difficulty, by oxidizing the solid product under the same condition. When boiled with 47 percent nitric acid the solid product yielded nitro-compounds of high molecular weight, together with a little benzoic acid. Kaufmann considered this solid essentially aliphatic, as distinguished from the aromatic substance cuprene obtained by heat polymerization of acetylene in the presence of copper.

Epner[58] claimed that liquid motor fuels might be obtained from acetylene by passing the gas through an alternating current field of high tension, with frequency above 500 cycles, and preferably of the order of 10,000 cycles, at a temperature higher than the boiling point of the product.

In studying the hydrogenation of hydrocarbons under influence of the electric discharge, Volmar and Hirtz[201] submitted acetylene in the presence of hydrogen to a discharge at 10,000 volts. The acetylene readily polymerized and the hydrogen acted on both the acetylene and its polymers, giving a complex mixture. Acetylenic substances to C_{10} and saturated hydrocarbons to C_8 were reported. Reduction of pressure decreased the polymerization, while the yield of higher saturated and olefinic hydrocarbons increased with reduction in hydrogen. The polymerization was thought to be preceded by activation of acetylene.

Lind and Schultze[128] made a series of runs at low pressure with varied times of exposure to the discharge for information regarding the mechanism of condensation. Explaining the reaction as preceded by a clustering of molecules they concluded that as soon as an ionized molecule was formed the reaction to a solid took place quickly. (They term the brown, solid product, "cuprene," although it seems not to have been proved identical with the product of heat in the presence of copper, and there is some evidence that the two are not alike). Hydrogen was liberated during the reaction, but its amount did not increase by prolonging exposure to the discharge, nor was any produced by action of the discharge on the precipitated solid in the absence of gas. Traces of either ethylene or ethane were also found.

Lind and Schultze found that contrary to the result with alpha radiation, acetylene is in part hydrogenated when exposed with hydrogen to the electric

discharge. A solid product, ethane, propane and liquids form at the same time. In a second publication[129] they compared the results of an ozonizer type of discharge on acetylene and other hydrocarbons. Deposition of solid on the walls of the chamber retarded the reaction.

Harkins and Gans[84] found that when exposed to the electrodeless discharge acetylene formed an insoluble reddish-brown solid. There was no formation of gas. In the spectrum obtained there were bands indicating CH, C, C_2 molecules, C^+ ions, and H, which were the bands also given by benzene.

In the manufacture of cuprene the silent discharge is sometimes used while the acetylene is heated in the presence of copper.

F. Action of Alpha Particles.

Mund and Koch[153] introduced 58 millicuries of radon into one bulb of a differential manometer containing acetylene at about atmospheric pressure. They found that in 8 days the pressure decreased 278 mm. and traces of a voluminous brownish-yellow, amorphous powder deposited on the walls of the vessel. Later they[154] determined the rate of polymerization of acetylene containing approximately 5×10^{-5} percent radon, and found that each alpha particle emitted by the emanation caused the disappearance of 4.38×10^6 molecules of acetylene. Since 2.13×10^5 gaseous were ions produced, 20.5 molecules of acetylene disappeared for each ion pair formed. In further work[155] "no variation exceeding experimental error could be detected in the number of molecules of acetylene polymerized per pair of ions produced in the system (1) at different pressures; (2) at temperatures 0°C., 20°C. and 100°C.; and (3) in the presence of small quantities of air. The general mean value of eleven measurements obtained in the absence of oxygen, with two concordant results previously reported, gave 20.2 as ratio of the number of molecules of acetylene polymerized per pair of ions produced."

Lind and Bardwell[121] also found that exposure of acetylene to radium emanation produced a solid yellowish powder similar to "cuprene," and a small amount of hydrogen.

When an equal volume of nitrogen was mixed with the acetylene it accelerated the rate of polymerization, an effect termed "ionic catalysis." The nitrogen ions formed by the action of the α-particles from the radon apparently served as additional clustering and polymerization centers. Lind and Bardwell reported "that the number of acetylene molecules condensing for each N_2^+ ion is approximately 20, the same as for each $C_2H_2^+$ and polymerization by both routes proceeds simultaneously. In other words $\dfrac{-M(C_2H_2)}{N(C_2H_2+N_2)} = 20.$"

($-M$ is the number of acetylene molecules disappearing, N the number of ions.)

Further experiments of Lind and Bardwell[122] in which "helium, neon, and argon were separately mixed with acetylene and a small quantity of radon was introduced as ionizing source" gave "the same results as for nitrogen; the ratios;

$$\frac{-MC_2H_2}{N(C_2H_2+He)}, \frac{-MC_2H_2}{N(C_2H_2+Ne)} \text{ and } \frac{-MC_2H_2}{N(C_2H_2+A)}$$

were all initially equal to about 20, the value for $\dfrac{-MC_2H_2}{NC_2H_2}$ in the case of pure acetylene. This value is maintained even when the ionization of the inert is as much as 50 percent of the total."

Extension of the study of inert gases as "ionic" catalysts[123,124] showed that krypton and xenon also catalyzed the polymerization of acetylene. Carbon dioxide had a similar effect, but in this case the ratio

$$\frac{-MC_2H_2}{N(C_2H_2+CO_2)} \text{ was } 17.4$$

As a mechanism for the polymerization of acetylene Lind, Bardwell and Perry[125] stated that "the simplest assumption is that a cluster containing at least 19 neutral molecules of acetylene is formed around each $C_2H_2^+$, and that the free electron (which has no affinity for neutral acetylene) finally neutralizes the cluster, which owing to the number of unsaturated valences then becomes stabilized as a polymer which precipitates as a solid

$$C_2H_2^+ + 19\ C_2H_2 \longrightarrow (C_2H_2)_{20}^+ + (-) \longrightarrow (C_2H_2)_{20}''$$

Because of failure to find a solvent for the yellowish solid polymer these investigators were unable to determine its molecular weight. The fact that neither oxygen, which would be expected to act as a inhibitor, nor other gases, which would be expected to be positive catalysts, affected the ion yield, supports a clustering rather than a chain mechanism.

G. *Action of Cathode Rays.*

High-voltage electrons from a cathode ray tube provided with an aluminum window acting on acetylene produce a yellow substance similar to the product obtained with the corona discharge or with radium emanation. Coolidge[50] first reported this action.

McLennan, Perrin, and Treton[137] bombarded acetylene with high-speed electrons in a cathode ray tube similar to that described by Coolidge.[51] No change in pressure occurred until the voltage exceeded 85 kilovolts, when a slight mist formed throughout the reaction coil and a pale yellow amorphous solid deposited on the walls. Reaction was accompanied by a decrease in pressure. The yellow solid had no measurable vapor pressure and on bombarding it there was no increase of pressure. The reaction appeared unimolecular, as the rate of change of pressure was proportional to the pressure for any given voltage, and the velocity coefficient increased directly as the voltage.

The number of electrons passing through the window of the cathode ray tube was determined by collecting them in a Faraday cylinder and measuring the current. It was found that the number of molecules of acetylene reacting was of the same order as the number of ions formed by the electrons passing through the window.

A. L. Marshall reported[135] that when acetylene gas was exposed to cathode rays a white cloud rapidly filled the whole chamber, and fluffy white yellow

powder deposited on the walls. Apparently the reaction was exclusively polymerization, with no elimination of hydrogen. The rate of disappearance of acetylene was approximately proportional to the acetylene pressure. Dilution of acetylene with nitrogen considerably increased the rate of reaction over that of acetylene alone at a pressure equal to the partial pressure of acetylene in the mixture.

When heating the acetylene during the raying, it was found that the yield was not altered, but as the temperature rose the powder appeared to increase in density, and changed in color from light yellow to chocolate brown at 400°. Marshall decomposed the yellow powder by heating it in an evacuated system, but obtained erratic results, which he attributed to the fact that the polymer had absorbed a considerable proportion of oxygen. He found that it would take up about 30% of its weight of oxygen on standing in air.

H. *Action of Light.*

There has been considerable interest in the action of light on acetylene, from the standpoint of the product obtained, the wave-length of the effective light and the quantum yield. Lind[120] points out the interest in comparing in the case of acetylene, the photochemical reaction and the ionization reactions, such as produced by alpha particles. In both cases the primary step is activation, involving a single electron in a single molecule. Formation of a gas ion involves complete removal of an electron from the molecule, while photochemical activation is attributed to the shift of an electron from its normal orbit to one of higher energy.

In both ionic and photo-reactions, changes normally requiring high temperature are brought about at room temperature. In ionization changes, clustering appears to be the first step. This prevents a chain reaction, and also enables the molecules to withstand the shattering effect of ionizing forces. In photochemical change clustering about an excited molecule is also assumed.

Lind and Livingston[126,127] investigated the quantum yield in the photochemical polymerization of acetylene. They exposed the hydrocarbon in a glass vessel at constant temperature to radiation from a "hot" mercury vapor arc. The product was a brown, inert solid believed to be cuprene. The reaction appeared to occur in one step, with no side reactions or gaseous products. The reaction velocity was proportional to the pressure as long as this did not exceed 30 cm. of mercury, and approached a constant value at higher pressures. This was interpreted as indicating that the rate of polymerization was proportional to the intensity of the absorbed light. The temperature coefficient of the change was 1.25 per 10°, which may have been simply the coefficient of light adsorption. Experiments with screens of varied ultra-violet transparency showed that light of 2537 Å and longer was not effective in causing polymerization, probably because acetylene does not absorb these wavelengths. The quantum yield found (ratio of molecules polymerized to light quanta absorbed) was 9.2 ± 1.5. The investigators drew attention to the fact that this was about half the yield per ion pair in polymerization by the action of alpha particles, or approximately equal to the average yield per ion.

Bone and Wilson[35] found that pure acetylene exposed to bright sunlight in glass bulbs for two or three days gave a faint brown deposit which increased in thickness and became darker as the exposure was prolonged. No deposit formed in a portion of the tube which was protected from the light. Besides unchanged acetylene the residual gas contained about two percent of a "fairly dense hydrocarbon" (not saturated) possibly mixed with a small quantity of hydrogen.

D. Berthelot and H. Gaudechon[21,22,28] observed that exposure of acetylene to ultra-violet light from a mercury vapor lamp for several seconds caused precipitation of a yellowish-brown, waxy solid. The polymerization of acetylene was not accompanied by decomposition nor by formation of benzene. The reaction was not modified by the presence of hydrogen or nitrogen in the acetylene. It was stated, however, in contradiction to Bone and Wilson, that exposure of acetylene to sunlight for one year in thin quartz tubes produced neither change in volume nor polymerization.

Bates and Taylor[4] reported that acetylene was polymerized to the yellow solid "cuprene" both by ultra-violet light and by excited mercury atoms. The rate of reaction was increased by cooling the vertical Cooper-Hewitt arc used by immersion in running water.

When a hydrogen-acetylene-mercury mixture was illuminated by the cooled arc, "cuprene" was deposited on all portions of the reaction vessel except that adjacent to the arc, which became coated with a colorless oil. The cuprene which condensed in this region was apparently immediately acted upon by hydrogen atoms. The resulting gas was made up of 95.7 percent hydrogen and 4.3 percent unsaturated hydrocarbons.

Reinicke[171] reported that while sunlight, or light from an incandescent lamp or an iron arc did not change acetylene, it was polymerized even in absence of air or moisture when illuminated by a quartz mercury arc at pressures of one to ten atmospheres. The product was a yellow amorphous solid insoluble in most solvents. The polymerization was not a heat effect, as it went on even when the vessel containing the acetylene was cooled to 12°. The rays causing the action were of a shorter wave-length than 3000 Å, as the polymerization was stopped when uviolglass screened the source of light. When the acetylene was confined over a solution of copper salts, radiation gave rise to low-melting colorless crystals, in addition to the amorphous solid. These crystals appeared to be a formaldehyde polymer. They were thought to be the same as the crystalline product of Thiele[198] who reported contraction and an unidentified white precipitate on exposure of acetylene to light from a quartz lamp. Carbon, said by Romer[178] to be formed from acetylene by the action of light, was in no case observed.

·I.   *Action of Canal Rays.*

Kinoshita[113] subjected acetylene to the action of canal rays, using an exposure of three hours with 2000 volts at 1-3 milliamperes. Carbon was de-

posited on the walls and the gas pressure dropped, probably as a result of polymerization. The accompanying spectrum plainly showed C and H lines.

J. *Action of Electromagnetic Field.*

Moens and Juliard[148] found that acetylene was rapidly polymerized to a yellowish white powder when exposed to electromagnetic fields of high frequency.

II. Rearrangement of Higher Acetylenes

Under the influence of heat and alkaline reagents a number of acetylenes have been found to rearrange. Acetylenes having the triple bond with the 1-position change to isomers having the triple bond in the 2-position and these, by a change in method, may be reconverted into derivatives of the 1-alkalines. This sort of shift,

$$R-CH_2-C\equiv CH \longrightarrow RC\equiv C-CH_2$$
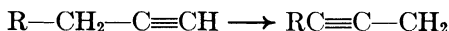
resembles the commonly occurring shift in a three-carbon system

$$R-CH_2-CH=CH_2 \longrightarrow RCH=C-CH_2$$
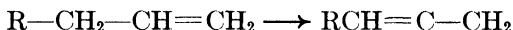
and both are in a sense analogous to the rearrangement in ketoenol tautomerism.

The most complete work on rearrangement of this type is that of Faworsky.[60] He found that ethylacetylene, on 16 hours heating in a sealed tube with alcoholic potash at 170° was converted into dimethylacetylene. This with slightly diluted sulfuric acid formed hexamethylbenzene. Other monosubstituted acetylenes which he investigated underwent a similar shift. Thus propylacetylene gave methylethylacetylene on treatment with alcoholic potash for 24 hours at 170°. The disubstituted acetylene did not polymerize with sulfuric acid. This isomerization was also brought about by alcoholic soda and by sodium alcoholate. Faworsky proposed a mechanism involving addition of alkali alcoholate followed by loss of alcohol to form an allene and further reaction with alcoholate. He postulated that such acetylenes as isopropylacetylene would go only as far as the allene stage, and confirmed this by experiment (isopropylacetylene gave dimethylallene). The behavior of ter-butylacetylene, also accorded with his mechanism, as even under extreme conditions alcoholic potash produced no change.

In his second paper, Faworsky[61] reversed the shifts previously studied by contact of the 2-acetylene with sodium. Methylethylacetylene gave the sodium derivative of propylacetylene, methylpropylacetylene gave butylacetylene, dimethyl allene gave isopropylacetylene. He[62] also found that methylacetylene on heating with alcoholic potash did not go, as might have been expected, to allene, but was in part converted into an unsaturated ether $CH_3C(OC_2H_5) = CH_2$, which he considered the first step in his rearrangement mechanism. Further change to allene was blocked by the resistance of the methyl hydrogens to removal to form alcohol.

Further work[63] showed that amyl and hexylacetylenes underwent rearrangements of this type.

Behal[6] obtained methylbutylacetylene when heptine-1 was heated at 140° to 150° with alcoholic potash for 24 hours.

Wislicenus and Schmidt[203] found that rearrangement by alcoholic alkali was not always complete, some ethylacetylene remaining even after most of it had been converted into dimethylacetylene.

Bourguel[37] studied the reverse rearrangement by which 2- and even 3-acetylenes were converted into sodium derivatives of the 1-acetylenes by action of sodamide. He found this change to take place with butine, pentine, octine, and nonine.

By passing a mixture containing 80 percent of heptine-1 over. soda lime in an iron tube heated to 380°, Guest claimed that rearrangement to heptane-2 proceeded to the extent of 70 percent. At 250° no rearrangement occurred, nor was there any significant change at 350° without the contact agent. The reverse change was brought about by heating with sodamide. The mixture obtained from the rearrangement over soda lime, which was reported to contain upwards of 80 percent heptine-2, was heated for twelve hours at 160° with finely divided sodamide suspended in 35 cc. of mineral oil. After washing and distilling, the final product contained 64 percent of heptine-1.

Hurd[93] believes that many of these rearrangements do not go completely from the 1-acetylene to the 2-acetylene stage, but stop with the allene. Rearrangement to the allene would involve disappearance of the active acetylenic hydrogen, which has been used as a criterion of rearrangement, and the allenes could easily be mistaken for 2-acetylenes.

III. Methylacetylene

The pyrolysis of methylacetylene was investigated by Meinert and Hurd.[138] The dry gas was passed through an electrically heated vertical pyrex tube at from 500° to 650°. Largely liquid products were produced at 575°, 88 percent of the hydrocarbon which was changed being converted into liquids. When the temperature was raised to 575°, ethylene, methane and hydrogen increased, and liquid products dropped to 61 percent. The liquids contained no aromatic hydrocarbons, and were therefore radically different from the polymerized products of acetylene, while they closely resembled the liquid produced by allene pyrolysis. It was therefore supposed that pyrolysis began by a conversion of methylacetylene to allene.

A summary of this work is given in Table III.

The liquids, boiled from 60°-215°, were not aromatic, and decolorized bromine. Apparently they consisted of polymers such as were formed from allene—a dimer, a tetramer and higher substances.

Absorption of methylacetylene in sulfuric acid followed by distillation, was found by Schrohe[193] to convert it into mesitylene.

TABLE III

Pyrolysis of Methylacetylene

(Meinert and Hurd)

Temperature °C.	550	575	650
Contact time, seconds	76	48	30
Volume entering gas, l.	13.05	6.73	2.13
Volume exit gas, l.	7.92	3.77	1.76
Analysis of exit gas, % by volume			
Acetylene	52.0	48.0	14.0
Allene[a]	18.6	16.8	11.8
Ethylene	3.6	3.0	23.1
Hydrogen	6.8	5.9	18.9
Paraffins	11.6		27.6
n in C_nH_{2n+2}	1.34		1.17
Extent of pyrolysis, %	64.5	67.	87.
Gaseous products formed per liter methylacetylene pyrolyzed, cc.			
Allene[a]	192	159	125
Ethylene	37.1	28.5	246
Hydrogen	72.0	57.0	201
Paraffins	123.0		294
Liquid yield, % of methylacetylene pyrolyzed	58.8	88.0	61.0

[a] "allene" may include some propylene.

IV. Dimethylacetylene

The formation of dimethylacetylene from ethylacetylene and its conversion by sulfuric acid and heat into hexamethylbenzene by Faworsky[60] has already been mentioned.

V. Ethylacetylene

Hurd and Meinert[94] passed ethylacetylene through a vertical pyrex tube, as in the pyrolysis of methylacetylene. The hydrocarbon was quite stable at 500°, only 23 percent decomposing with a contact time of 35 seconds. At 580° with the same contact time, conversion was complete. Less liquid and more gas were produced than was the case with methylacetylene.

Data from their runs are given in Table IV:

TABLE IV

Pyrolysis of Ethylacetylene

(Hurd and Meinert)

Temperature o°C.	500	550	580	600
Contact time, seconds	34.8	34.5	35.0	30.0
Percentage decomposition	22.6	47.0	95–100	95–100
Wt. of liquid formed, g.	1.5	4.0	6.7	6.0
Liquids formed % by wt. of				
ethylacetylene pyrolyzed	43.0	53.0	36.5	36.6
Analysis of off-gas, % by volume				
Carbon dioxide	83.0	22.4	7.3	5.0
Acetylenes	—	15.6	12.8	9.4
Gas soluble in 82.5% H_2SO_4	—	7.8	8.7	7.6
Ethylene	—	6.6	9.7	10.8
Hydrogen	—	4.6	13.6	17.0
Paraffins	—	37.4	40.1	43.4
n in C_nH_{2n+2}	—	1.49	1.23	1.18
Gaseous products formed per liter				
of ethylacetylene pyrolyzed, cc.				
Acetylenes		88.4	110	94.2
Gas soluble in 82.5% H_2SO_4		43.9	76.5	76.2
Ethylene		33.8	83.8	108
Hydrogen		26.0	118	170
Paraffins		211.0	346	435

A study of the off-gas indicated that acetylene itself made up at least 80 percent of the "acetylenes" reported, while the gases absorbed in 82.5 percent sulfuric acid were almost entirely propylene, with possibly small amounts of allene, but no methylallene.

About half of the liquid products boiled from 30° to 200°. The liquids were not aromatic, and while they were not identified they resembled those formed by pyrolysis of methylallene, allene, and methylacetylene.

VI. Pentine

Bouchardt[36] reported that "valerylene" (b.45–50°) a mixture of pentine isomers prepared from amyl alcohol (the alcohol a fermentation product) was polymerized by heating at 250°. That portion of the product boiling between 170° and 190° consisted mainly of "divalerylene."

VII. Heptine

Renard[172] pyrolyzed a heptine boiling at 103°-105° by passing the vapors through an iron tube one meter long, heated to "redness visible only in the dark." He obtained per liter of the hydrocarbon, 37 liters of gas, 720 cc. of brownish-yellow liquid, and about two grams of carbon. The gas consisted of hydrogen mixed with small quantities of unidentified hydrocarbons. From the liquid, Renard isolated 20 to 25 cc. of a pentine, 100 to 110 cc. of a hexine (boiling at 70° to 73°), 20 to 25 cc. of benzene, and 180 to 200 cc. of toluene. Of the fraction which distilled above 115°, about half came over below 180°, and left a thick residue, solid at ordinary temperatures, which was said to contain no aromatic hydrocarbons. Renard concluded that under the influence of heat, heptine decomposed primarily into hydrogen and toluene, with a small amount of a pentine and a hexine. The benzene was considered to arise from the hexine.

By exposing heptine-1 to the action of the silent electrical discharge *in vacuo*, Losanitch[132] obtained "diheptine," whose formula was given as

$$(CH_3(CH_2)_4C : CH)_2,$$
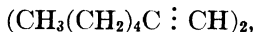
a colorless, mobile liquid miscible in alcohol, ether, and benzene; triheptine, a thick, odorous liquid soluble in ether and in benzene; and "undecaheptine," a dark red, thick mass also soluble in ether and benzene.

VIII. Octine

Losanitsch[132] reported that the action of the silent electrical discharge converted octine-1 into "dioctine," $(C_8H_{14})_2$, a colorless liquid soluble in alcohol, ether, and benzene; and "nonaoctine," $(C_8H_{14})_9$, a dark red, soft mass soluble in ether and benzene but insoluble in alcohol.

IX. Hexadiine-2, 4

Vapors of dimethyl diacetylene $CH_3C : C . C : C . CH_3$ subjected suddenly to red heat were found, by Griner[78] to decompose, leaving a residue of carbon. This compound is stable, as it withstands shock and gradual heating to high temperatures without explosion.

X. Vinylacetylene and Divinylacetylene

The polymerization of these substances by heat as reported by Nieuwland, Calcott, Downing, and Carter,[158] and by Collins[46] has been discussed in the section "Acetylene; Action of Chemical Reagents."

Heisig[85] reported that on exposure to the action of alpha particles from radon, vinylacetylene condenses to a white solid, which becomes orange on continued exposure. About eleven molecules of the hydrocarbon polymerize per ion pair formed. Practically no hydrogen or methane is evolved.

XI. Summary Tables

Acetylene

Action of Heat—Non-Catalytic

Temperature

300-800°   Largely polymerization, optimum 600-700°. Products are aromatic hydrocarbons in great variety, with some olefins and paraffin hydrocarbons.

The presence of carbon promotes smooth reaction. In upper portion of this temperature range, some decomposition to carbon, hydrogen, and methane occurs.

800-1000°   Both decomposition and polymerization occurring, the former taking ascendency.

1000° and above Almost exclusively decomposition to carbon, hydrogen, and methane. Some acetylene in equilibrium with these at above 1700°.

Catalytic

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Aluminum	Hilpert[88]	400°	Carbon, tar
	Kusnetsov[116]	About 659°	Decomposition—Carbon hydrogen, aluminum carbide
	Hodgkinson[89]	About 659°	Carbon
Beryllium	Durand[55]	450°	Decomposition, some polymerization. Carbon, beryllium acetylide
Cadmium	Hodgkinson[89]	321°	Carbon, acetylide
	Durand[55]	500°	Carbon, acetylide
Cobalt	Moissan and Moureu[149,151]	Room	Metal becomes incandescent Carbon, hydrogen, tar rich in benzene
	Sabatier and Senderens[186,188]	Above 200°	Carbon
	Tiede and Jenisch[199]	380°	Carbon
		480°	Oil
	Fischer, Peters and Koch[66]	300°	Methane
Copper	Erdmann and Köthner[59]	To 180°	Polymerization-liquids,
		230°	Cuprene, carbon
		400-500°	Decomposition—carbon

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
	Catalytic (Continued)		
Copper (Cont'd)	Gooch and Baldwin[76]	225-250°	Cuprene
	Alexander[1]	225-250°	Cuprene, heavy tar
		Over 260°	Carbon
	Sabatier and Senderens[180,181,182,188]	180°-250°	Olefinic and aromatic liquid, cuprene, hydrogen, ethane, gaseous olefins
	Hilpert[88]	—	Brown deposit
	Kaufmann and Schneider[110]	—	Cuprene Oily liquid
	Kaufmann and Mohnhaupt[109]	230-300°	Cuprene
	Schläpfer and Stadler[192]	300°	75-80% cuprene 55-57% aromatic tar 13-17% gas
	Tiede and Jenish[199]	310°-600°	Oil
	Erdmann[57]	400°-500°	Graphite
	Berl and Hofmann[8]	580°	Carbon
	Hodgkinson[89]	1038°	Carbon
Gold	Durand[55]	500°	Carbon
Iron	Berthelot[11,12,14]	—	Reaction began at lower temperature than without catalyst Carbon, hydrogen, "empyreumatic hydrocarbons
	Ramsay[169]	Red heat	Oil, apparently benzene
	Moissan and Moureau[149,151]	Room	Pyrophoric metal became incandescent. Carbon, hydrogen, liquid rich in benzene
	Sabatier and Senderens[186,188]	Room	Carbon, hydrogen, ethane, olefins, aromatic liquid
	Hilpert[88]	300°-400°	Carbon
	Hodgkinson[89]	To 1050°	Carbon
	Tiede and Jenisch[199]	400°	Carbon formation began
		540°	Oil formation began
		600°	Very little oil—rapid decomposition to carbon and hydrogen
	Bradley and Parr[38]	725°	Complete decomposition
	Rimarski and Konschak[176]	600°-900°	Almost complete decomposition
	Fischer, Peters and Koch[66]	300°-400°	9% acetylene 91% hydrogen, gave both oil and carbon

Catalytic (Continued)

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Iron (Cont'd)	Berl and Hofmann[8]	580°	Largely formation of carbon
	Erdmann and Köthner[59]	—	Aided oil formation
Lead	Hilpert[88]	327°-500°	Carbon, no benzene formation
	Hodgkinson[89]		Same
Lithium	Tiede and Jenisch[199]	—	Carbon, hydrogen, acetylide
Magnesium	Berthelot[10]	—	Acetylide
	Moissan[150]	—	Carbon, carbide
	Keiser and McMaster[111]	—	Magnesium allylide and carbide
	Novak[159,160,161]	400°-700°	Carbide and allylide, carbon
Manganese	Tiede and Jenisch[199]	440°	Carbon separation
		480°	Oil formation
		600°	Largely decomposition to carbon and hydrogen
Mercury	Hilpert[88]	—	Carbon
	Durand[55]	500°	Carbon
Nickel	Sabatier and Senderens[183,185,187,188]	Room	Liquid containing paraffins, olefins and aromatics from acetylene-hydrogen mixture
			Metal becomes incandescent
		Room	Metal incandescent—carbon, hydrogen, liquid rich in benzene
		180°	Lowest reaction temperature of nickel was free of hydrogen
		250°	Rapid reaction, decomposition, polymerization and hydrogenation. Paraffins, naphthenes, olefins, aromatic hydrocarbons formed
	Moissan and Moureu[149,151]	180°-300°	Slow reaction to cuprene
	Charitschkow[43]	300°	Acetylene + hydrogen gave liquid product
	Tiede and Jenisch[199]	360°	Carbon separated
		520°	Soil formed
	Hilpert[88]	300°	Carbon formed rapidly if iron was also present

Catalytic (Continued)

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Nickel (Cont'd)	Hodgkinson[89]	200°	Reaction noted—carbon formed
		600°	Rapid reaction
Palladium	Zelinsky and Kasansky[213]	300°	Carbon and a small amount of unsaturated condensate
	Durand[55]	500°	Carbon
Platinum	Moissan and Moureu[149-151]	Room	Metal becomes incandescent Carbon, hydrogen, liquid rich in benzene
	Sabatier and Senderens[181,186,188]	150°	Carbon and hydrogen, ethane, ethylene, benzene, styrene, reduced naphthalene and anthracene
	Schützenberger[194]	—	Carbon
	Lewes[117]	1000°	Ethylene, small amount of hydrogen and paraffins, oil, carbon
	Grehant[77]	—	Carbon
	Zelinsky and Kasansky[213]	300°	Liquid
		650°	Tar
Rubidium	Erdmann and Köthner[59]	—	Carbon
Sodium	de Forcrand[52]	Dull red	Sodium carbide, carbon
	Tiede and Jenisch[199]	—	Sodium acetylide, hydrogen and carbon
Tin	Bahr[3]	Below 475°	Aided polymerization
Uranium	Durand[55]	500°	Carbon
Potassium	Berthelot[10]	—	Gentle heating gave acetyline, carbon, hydrogen
	Moissan[150]	Room	Acetylide
Zinc	Erdmann and Köthner[59]	—	Apparently carbon deposited
	Hodgkinson[89]	To 419°	No significant action
	Hilpert[88]	Over 419°	Carbon, tar

The following additional metals were reported by Tiede and Jenisch[199] to have no effect on acetylene pyrolysis.

Antimony	Silver
Bismuth	Silicon
Boron	Tantalum
Cadmium	Thallium
Calcium	Titanium
Chromium	Tungsten
Molybdenum	Zirconium

Oxides

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Ferric oxide	Gooch and Baldwin[76]	150°-360°	Carbon
Silver oxide	Gooch and Baldwin[76]	Room	Explosive reaction, silver
Calcium oxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Stannic oxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Silicon dioxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Ceric sulfate	Comp. gén. deProduits de Synthèse[47]	80°	Polymerization
Ferric nitride	Hodgkinson[89]	—	Carbon
Ferrous sulfide	Bahr[3]	300°	Oil formed
		430°	Carbon separation as well as oil
	Fujio[73]	—	Increases low-boiling constituents in tar
Nickel carbonyl	Binnie[29]	190°	Low boiling unsaturated oil
Phosphoric acid	Bahr[3]	470°-480°	Carbon
Sodium and potassium hydroxide	Fry, Schultze, Weitcamp[72]	325°	Carbon, hydrogen, methane
Stannous chloride	Bahr[3]	500°	Little change

Action of Chemical Reagents

Reagent	Reference	Conditions and Results
Cuprous chloride	Nieuwland, Calcott, Downing and Carter[158]	Room temp. produced vinyl acetylene, divinyl acetylene, and an acetylene tetramer
Aluminum chloride	Baud[5]	70°-130°	Anthracene and high boiling unidentified hydrocarbons

Action of Electric Discharge

Reference	Conditions and Results
Mignonac and St. Aunay[144]	At 80°, dipropargyl, methylpentadiine, divinyl acetylene
de Wilde[54]	Yellow liquid changing to solid
Thénard[197]	Liquid and solid polymers
Berthelot[15,16,17]	Brown liquid, brown solid, hydrogen, ethane, ethylene
Schützenberger[195]	Resinous solid
Jackson and Northall-Laurie[103]	Brown solid

Action of Electric Discharge (Continued)

Reference	Conditions and Results
Losanitsch[130,131,132,133]	Brown liquid turning to solid. In vacuo some carbon and hydrogen also
Jovitschitsch[105,106]	Insoluble solid
Kaufmann[108]	Viscous liquid and solid, apparently aliphatic
Lind and Schultze[128]	Solid, termed cuprene, hydrogen, ethylene or ethane. With hydrogen, ethane, propane and liquids
Volmer and Hirtz[201]	Acetylene with hydrogen gave higher acetylenes, olefins and paraffins

Action of Alpha Particles

Mund and Koch[153]	Yellow solid—variation in temperature and pressure did not change results
Lind and Bardwell[121,122,123,124]	Yellow solid—like cuprene

Action of Cathode Rays

Coolidge[50]	Yellow solid
McLennan, Perrin, Treton[137]	Yellow amorphous solid
Marshall[135]	Yellow to brown powder, depending on temperature

Action of Light

Bone and Wilson[35]	Sunlight, brown solid, trace of gaseous product
Berthelot and Gaudechon[21,22,23]	Ultra-violet gave yellowish-brown waxy solid. Sunlight had no effect
Bates and Taylor[4]	Ultra-violet or excited mercury atoms gave yellow solid, and liquid oil
Lind and Livingston[126,127]	Ultra-violet gave a brown inert solid. Effective wave-length below 2537 Å
Reinicke[171]	Ultra-violet gave yellow insoluble solid

Action of Canal Rays

Kinoshita[113]	Carbon, signs of polymerization

Action of Electro-Magnetic Field

Moens and Juliard[148]	Yellow-white powder

Methylacetylene

Reference	Conditions	Products
Meinert and Hurd[138]	Heat at 500°-650°	Largely unsaturated liquids. Some hydrogen, gaseous olefins, and paraffins
Schrohe[193]	Sulfuric Acid	Mesitylene

Dimethylacetylene

Reference	Conditions	Products
Faworsky[60]	Heat and sulfuric acid	Hexamethylbenzene

Ethylacetylene

Hurd and Meinert[94]	Heat at 500°-600°	Unsaturated liquids, gaseous olefins, paraffins, and hydrogen

Pentine

Bouchardat[36]	Heat at 250°	Dimer and other polymers

Heptine

Renard[172]	Dull red heat	Pentine, hexine, benzene, toluene, hydrogen and unidentified gaseous hydrocarbons
Losanitsch[132]	Silent discharge	Polymers—diheptine and higher

Octine

Losanitsch[132]	Silent discharge	Polymers, dioctine and higher

Hexadiine-2, 4

Griner[78]	Red heat	Carbon

Vinylacetylene and Divinylacetylene

Nieuwland, Calcott Dunning, Carter[158]	Heat and catalysts	Drying oils and resins
Collins[46]	Heat and catalysts	Drying oils and resins
Heisig[85]	Alpha particles	White to orange solid

XII. References

[1] Alexander: Ber., **32**, 2381-4 (1899).
[2] Alexejew: Izvestiya. Pedagog. Schelaputin Inst. Moscow, **4**, 1267 (1915); Chem. Zentr., 1925 II, 1588.
[3] Bahr: Ges. Abhandl. Kenntnis Kohle, **8**, 283 (1924-7), published (1929).
[4] Bates and Taylor: J. Am. Chem. Soc., **49**, 2438-56 (1927).
[5] Baud: Compt. rend., **130**, 1319-22 (1900).
[6] Behal: Bull., **49**, 581-4 (1888).
[7] Berger and Wirth: Ger. 92,801.
[8] Berl and Hofmann: Z. angew. Chem., **44**, 259 (1931).
[9] Berthelot: Compt. rend., **54**, 1044 (1862); Ann. Chim. Phys., (3) **67**, 70 (1863).
[10] Berthelot: Ann. Chim. Phys., (4) **9**, 402-7 (1866).
[11] Berthelot: Ann. Chim. Phys., (4) **9**, 445-69 (1866); Berthelot: "Les Carbures d'Hydrogène," **1**, 83-9 (1901).
[12] Berthelot: Bull., (2) **6**, 268-72 (1866).
[13] Berthelot: Compt. rend., **63**, 479, 515 (1866); Ann. Chim. Phys., (4) **12**, 52-81 (1867).
[14] Berthelot: Compt. rend., **62**, 905 (1866).

[15] Berthelot: Ann. Chim. Phys., (5) **10**, 67 (1877); "Les Carbures d'Hydrogène" **1**, 51, 117 (1901).

[16] Berthelot: Compt. rend., **111**, 471-2 (1890); Ann. Chim. Phys., (6) **24**, 135-7 (1891).

[17] Berthelot: Compt. rend., **126**, 570 (1898).

[18] Berthelot: Ann. Chim. Phys., (7) **22**, 445 (1901).

[19] Berthelot: Ann. Chim. Phys., (8) **6**, 184 (1905).

[20] Berthelot: Compt. rend, **140**, 910 (1905).

[21] Berthelot and Gaudechon: Compt. rend., **150**, 1169-72 (1910).

[22] Berthelot and Gaudechon: Rev. gén. sci., **22**, 330 (1911).

[23] Berthelot and Gaudechon: Compt. rend., **155**, 207-10 (1912).

[24] Berthelot and Le Chatelier: Compt. rend., **129**, 427 (1899); Ann. Chim. Phys., (7) **20**, 15 (1900).

[25] Berthelot and Vieille: Compt. rend., **123**, 523-30 (1896); Ann. Chim. Phys., (7) **11**, 501 (1897).

[26] Berthelot and Vieille: Compt. rend., **124**, 988 (1897); Ann. Chim. Phys., (7) **13**, 6 (1898); see Claude: Compt. rend., **124**, 626 (1897).

[27] Berthelot and Vieille: Compt. rend., **124**, 1002 (1897).

[28] Berthelot and Vieille: Compt. rend., **128**, 777 (1899); Ann. Chim. Phys., (7) **17**, 303 (1899).

[29] Binnie: J. Soc. Chem. Ind., **50**, 297-9 (1931).

[30] Bone and Cain: Chem. News, **74**, 268 (1896); Proc. Chem. Soc., **12**, 177 (1896).

[31] Bone and Coward: J. Chem. Soc., **93**, 1197 (1908); Proc. Chem. Soc., **24**, 167 (1908).

[32] Bone and Jerdan: J. Chem. Soc., **71**, 41 (1897).

[33] Bone and Jerdan: J. Chem. Soc., **71**, 59-60 (1897).

[34] Bone and Jerdan: Proc. Chem. Soc., **17**, 164 (1901).

[35] Bone and Wilson: Proc. Chem. Soc., **14**, 155-6 (1898).

[36] Bouchardat: Compt. rend., **90**, 1560-3 (1880).

[37] Bourguel: Ann., **10**, 3, 325 (1925).

[38] Bradley and Parr: Chem. Met. Eng., **27**, 737-44 (1922).

[39] Bullier: Bull., (3) **17**, 646-54 (1897).

[40] Burrell and Oberfell: Bur. Mines Tech. Paper, **112**, 11-12 (1915).

[41] Campbell: Am. Chem. J., **17**, 690 (1895).

[42] Caro: Verh. Ver. geförderung Gewerbefleisses, **85**, 205-236, 245-292 (1906).

[43] Charitschkow: J. Russ. Phys.-Chem. Soc., **38**, 880-1 (1906); Chem. Zentr., **88**, I, 294 (1907).

[44] Chemistry Industry, **20**, 53 (1897).

[45] Claude: Compt. rend., **128**, 303 (1899).

[46] Collins: U. S. 1,812,849, June 30, 1931.

[47] Compagnie Générale des Produits de Synthèse: Fr. 658,643, Aug. 6, 1928. Chem. Abs., **23**, 5305 (1929).

[48] Consortium Electrochemische Industrie: Fr. 59,333, Jan. 22, 1925, Aus. 103,106, Jan. 7, 1925.

[49] Constable: Nature, **122**, 882 (1928).

[50] Coolidge: Science, **62**, 441 (1925).

[51] Coolidge: J. Franklin Inst., **202**, 693 (1926).

[52] de Forcrand: Compt. rend., **120**, 1215-8 (1895).

[53] de Wilde: Bull., (2) **6**, 267 (1866).

[54] de Wilde: Ber., **7**, 357 (1874).

[55] Durand: Bull., **35**, 1141-4 (1924).

[56] Elektrizitätswerke Lonza Swiss, 95,237, May 7, 1921; Ger. 395,549, July 1, 1922; Brit. 200,087, June 22, 1921.

[57] Erdmann: Acetylene in Wiss. und Ind., **1**, 72 (1898).

[58] Epner: Fr. 654,449, May 19, 1928; Chem. Abs., **23**, 3795 (1929).

[59] Erdmann and Köthner: Z. anorg. allgem. Chem., **18**, 48-58 (1898); Köthner: Dissertation, Halle (1896).

[60] Faworsky: J. prakt. chem., (2) **37**, 384-395 (1888).

[61] (2) **37**, 417 (1888).

[62] (2) **37**, 531 (1888).

[63] (2) **44**, 208 (1891).

[64] Fischer, Bangert and Pichler: Brennstoff-Chem., **10**, 279-82 (1929).

[65] Fischer and Peters: Brennstoff-Chem., **12**, 286 (1931).

[66] Fischer, Peters and Koch: Brennstoff-Chem., **10**, 383-5 (1929).

[67] Fischer, Schrader and Ehrhardt: Ges. Abhandl. Kenntnis Kohle, **4**, 389, 393 (1919).

[68] Fowler and Mardles: Trans. Faraday Soc., **23**, 301-6 (1927).

[69] Francis and Kleinschmidt: Proc. Am. Petroleum Inst., **11**, Sect. III, 93-99 (1930); Francis: Ind. Eng. Chem., **20**, 277 (1928).

[70] Frank: Ger. 112,416.

[71] Frank: Z. angew. Chem., **18**, 1733-5 (1905).

[72] Fry, Schulze, and Weitkamp: J. Am. Chem. Soc., **46**, 2268-75 (1924).

[73] Fujio: J. Soc. Chem. Ind. Japan, **31**, 77-86 (1928); Chem. Abs., **22**, 2363 (1928).
[74] Gaud: Compt. rend., **134**, 175-7 (1902).
[75] Gerdes: Ann. für Gewerbe und Bauwesen, **40**, 1 (1897) see 4.
[76] Gooch and Baldwin: Am. J. Sci., (4) **8**, 354-8 (1899); Z. anorg. allgem. Chem., **22**, 235-40 (1900).
[77] Grehant: Compt. rend., **146**, 1199-1200 (1908).
[78] Griner: Ann. Chim. Phys., (6) **26**, 357 (1892).
[79] Gros: Brit. 211,461, Feb. 2, 1924:
[80] Gros: Ger. 475,883, Jan. 22, 1924.
[81] Guest: J. Am. Chem. Soc., **50**, 1744-6 (1928).
[82] Haber and Oechelhäuser: J. Gasbel., **39**, 830-34 (1896); Haber: "Experimental Untersuchungen uber Zerzetzung und Verbrennung von Kohlenwasserstoffen," 71-2 (1896).
[83] Hague and Wheeler: J. Chem. Soc., **1929**, 391.
[84] Harkins and Gans: J. Am. Chem. Soc., **52**, 5165 (1930).
[85] Heisig: J. Am. Chem. Soc., **53**, 4460 (1931).
[86] Hermann, Deutsch, and Haehnel: Can. 256,557, Dec. 22, 1925.
[87] Herzog: Chem. Ztg., **55**, 461, 478 (1931); Kunststoffe, **21**, 49 (1931).
[88] Hilpert: Ges. Abhandl. Kenntnis Kohle, **1**, 271-5 (1917).
[89] Hodgkinson: J. Soc. Chem. Ind., **37**, 86-7T (1918).
[90] Hostmann-Steinbergsche Farbenfabriken Ges: Brit. 341,235, Sept. 12, 1929.
[91] Horwitz: Ger. 205,705.
[92] Hubau: Ger. 103, 862.
[93] Hurd: Private Communication (1932).
[94] Hurd and Meinert: J. Am. Chem. Soc., **53**, 289 (1931).
[95] I. G. Farbenindustrie A. G.: Brit. 316,422, July 13, 1928.
[96] I. G. Farbenindustrie A. G.: Brit. 334,203, Feb. 23, 1929.
[97] I. G. Farbenindustrie A. G.: Brit. 346,680, Oct. 12, 1929.
[98] I. G. Farbenindustrie A. G.: Fr. 35,190.
[99] I. G. Farbenindustrie A. G.: Fr. 666,586, Dec. 31, 1928; Chem. Abs., **24**, 1476 (1930).
[100] I. G. Farbenindustrie A. G.: Fr. 666,611, Jan. 2, 1929; Chem. Abs., **24**, 1389 (1930).
[101] Ika and Ogura: J. Soc. Chem. Ind. Japan, **30**, 461-9 (1927); Chem. Abs., **21**, 3046-7 (1927).
[102] Ipatiev: Nat'l Petroleum News, **23**, No. 25, 61 (1931).
[103] Jackson and Northall-Laurie: Proc. Chem. Soc., **22**, 155 (1906).
[104] Janet: Z. Calc. Carb. und. Acet., **5**, 237 (1901).
[105] Jovitschitsch: Monatshefte, **29**, 1-14 (1908); Sitz. Akad. Wiss. Wien., **116**, IIb, 1241-54 (1907).
[106] Jovitschitsch: Bull. Sci. Acad. Roy. Belg., (5) **10**, 465 (1924).
[107] Jovitschitsch: Bull. Sci. Acad. Roy. Belg., (5) **13**, 365-70 (1927).
[108] Kaufmann: Ann., **417**, 34-59 (1918).
[109] Kaufmann and Mohnhaupt: Ber., **56**, 2533-6 (1923).
[110] Kaufmann and Schneider: Ber., **55**, 267-82 (1922).
[111] Keiser and McMaster: J. Am. Chem. Soc., **32**, 388-91 (1910).
[112] Kennaway: Brit. Med. J., **1925**, II, 1-4.
[113] Kinoshita: Physik. Z., **8**, 35 (1907).
[114] Körting: J. Gasbel., **42**, 843-8 (1899).
[115] Kovache and Tricot: Chimie et·Industrie, **13**, 361-72, 537-47 (1925).
[116] Kusnetzov: Ber., **40**, 2871 (1907).
[117] Lewes: Proc. Roy. Soc., **55**, 100-2 (1894).
[118] Lewes: J. Soc. Chem. Ind., **17**, 532 (1898).
[119] Lichtenhahn: Brit. 200,087, Can. 238,888, Mar. 25, 1924.
[120] Lind: J. Phys. Chem., **32**, 573 (1928).
[121] Lind and Bardwell: Science, **62**, 422-4 (1925).
[122] Lind and Bardwell: Science, **62**, 593-4 (1925).
[123] Lind and Bardwell: Science, **63**, 310-1 (1926).
[124] Lind and Bardwell: J. Am. Chem. Soc., **48**, 1575-1584 (1926).
[125] Lind, Bardwell and Perry: J. Am. Chem. Soc., **48**, 1556-75 (1926).
[126] Lind and Livingston: J. Am. Chem. Soc., **52**, 4613 (1930).
[127] Lind and Livingston: J. Am. Chem. Soc., **54**, 94 (1932).
[128] Lind and Schultze: J. Am. Chem. Soc., **53**, 3355 (1931).
[129] Lind and Schultze: Trans. Am. Electrochem. Soc., **1931**, 165.
[130] Losanitsch: Ber., **40**, 4656-66 (1907).
[131] Losanitsch: Sitz. Akad. Wiss. Wien, **117**, IIb, 467-76 (1908).
[132] Losanitsch: Bull. Soc. stiin. Bucharest, **23**, 3-33 (1914); Chem. Abs., **11**, 254 (1917).
[133] Losanitsch: Bull. Sci. Acad. Roy. Belg., (5) **11**, 325 (1925).
[134] Maquenne: Compt. rend., **121**, 424-7 (1895).
[135] Marshall: Private Communication (1930).
[136] Matignon: Compt. rend., **124**, 775-7 (1897).
[137] McLennan, Perrin and Treton: Proc. Roy. Soc., **125A**, 246-62 (1929).

[138] Meinert and Hurd: J. Am. Chem. Soc., **52**, 4540 (1930).
[139] Meyer: Ber., **45**, 1609-33 (1912).
[140] Meyer and Fricke: Ber., **47**, 2765-74 (1914).
[141] R. Meyer and W. Meyer: Ber., **51**, 1571-87 (1918).
[142] Meyer and Taeger: Ber., **53**, 1261-5 (1920).
[143] Meyer and Tanzen: Ber., **46**, 3183-99 (1913).
[144] Mignonac and de Saint-Aunay: Compt. rend., **188**, 959-61 (1929).
[145] Mixter: Am. J. Sci., (4) **9**, 1-9 (1900).
[146] Mixter: Am. J. Sci., (4) **10**, 299-309 (1900).
[147] Mixter: Am. J. Sci., (4) **12**, 347-57 (1901).
[148] Moens and Juliard: Bull. Sci. Acad. Roy. Belg., **13**, 201-5 (1927).
[149] Moissan: J. Franklin Inst., **143**, 147 (1897).
[150] Moissan: Compt. rend., **126**, 302 (1898).
[151] Moissan and Moureu: Compt. rend., **122**, 1240-3 (1896); Bull., (3) **15**, 1296 (1896).
[152] Morani: Ger. 141, 884.
[153] Mund and Koch: Bull. Soc. Chim. Belg., **34**, 119-26 (1925).
[154] Mund and Koch: Bull. Soc. Chim. Belg., **34**, 241-55 (1925).
[155] Mund and Koch: J. Phys. Chem., **30**, 289-93 (1926).
[156] N. V. de Bataafsche Petroleum Maatschappij, Brit. 344,470, Nov. 13, 1928.
[157] N. V. Electrozuurstof-en-Waterstoffabriek: Brit. 303,797, Jan. 8, 1929; Dutch 20,851, Nov. 15, 1929; Chem. Abs., **24**, 931 (1930).
[158] Nieuwland, Calcott, Downing and Carter: J. Am. Chem. Soc., **53**, 4197 (1931); See also Nieuwland: U. S. 1,811,959 and U. S. 1,812,541, June 30, 1929.
[159] Novak: Ber., **42**, 4209-13 (1909); See Lidov and Kusnetzov, J. Russ. Phys.-Chem. Soc., **37**, 804-3 (1905); Chem Zentr., **1906**, I, 329.
[160] Novak: Ceska adademia Trida II: Matematica-Prirodnicka Rozpravy, **18**, 50 (1909).
[161] Novak: Z. physik. Chem., **73**, 513-46 (1910).
[162] Pease: J. Am. Chem. Soc., **51**, 3470-5 (1929).
[163] Pictet: Ger. 255,733, Oct. 22, 1909; Chem. Abs., **6**, 145 (1912).
[164] Pictet: Brit. 24,256, Oct. 19, 1910.
[165] Pictet: Fr. 421,838, Oct. 26, 1910; J. Soc. Chem. Ind., **30**, 542 (1911).
[166] Pring and Fairlie: J. Chem. Soc., **99**, 1796 (1911).
[167] Pring and Hutton: J. Chem. Soc., **89**, 1591 (1906).
[168] Prudhomme: Brit. 238,931, Aug. 24, 1925.
[169] Ramsay: Phil. Mag., (5) **2**, 269 (1876).
[170] Rasch: Acetylene Wiss. und Ind., **4**, 180 (1900).
[171] Reinicke: Z. angew. Chem., **41**, 1144 (1928).
[172] Renard: Compt. rend., **104**, 574-6 (1887).
[173] Rimarski: Jahresberichte physikal. tech. Reichsanstalt, IV-VII.
[174] Rimarski: Autogene Metallbearbeitung, **22**, No. 10, 134; Acetylene in Wiss. und Ind., **32**, No. 5, 69-73; Chem. Abs., **23**, 4344 (1929).
[175] Rimarski: Z. angew. Chem., **42**, 933 (1929).
[176] Rimarski and Konschak: Acetylene Wiss. und Ind., **31**, 24-9 (1928); Chem. Abs., **22**, 2454 (1928).
[177] Rimarski and Konschak: Acetylene in Wiss. und Ind., **33**, 97 (1930); Acetylene in Sicherheitstechniker Hinsicht, **1925**, 73.
[178] Romer: Ann., **233**, 183 (1886).
[179] Rousseau: Compt. rend., **117**, 164 (1893).
[180] Sabatier: Assn. Française pour l'Avancement des Sciences **28**, I 235-6 (1899); IVe Congrès International de Chimie Appliquee, **1900**, III, 134-42.
[181] Sabatier-Reid: "Catalysis in Organic Chemistry," 329-332 (1923).
[182] Sabatier and Senderens: Bull., (3) **21**, 530 (1899); Compt. rend., **130**, 250-2 (1900).
[183] Sabatier and Senderens: Compt. rend., **128**, 1173-6 (1899); **130**, 1559 (1900).
[184] Sabatier and Senderens: Compt. rend., **131**, 40 (1900).
[185] Sabatier and Senderens: Compt. rend., **131**, 187-190 (1900); see Mailhe: Chem. Ztg., **32**, 244 (1908).
[186] Sabatier and Senderens: Compt. rend., **130**, 1628; **131**, 267-70 (1900); **134**, 1185 (1902).
[187] Sabatier and Senderens: Bull., (3) **25**, 678-84 (1901).
[188] Sabatier and Senderens: Ann. Chim. Phys., (8) **4**, 439-52 (1905).
[189] Salvadori: Gazz., **32**, II, 496 (1902).
[190] Sandman: Z. angew. Chem., **14**, 673 (1901).
[191] Schläpfer and Brunner: Helv. Chim. Acta, **13**, 1125 (1930).
[192] Schläpfer and Stadler: Helv. Chim. Acta, **9**, 185-99 (1926).
[193] Schrohe: Ber., **8**, 17 (1875).
[194] Schützenberger: "Traite de Chimie Generale," I, 723 (1880).
[195] Schützenberger: Compt. rend., **110**, 889-92 (1890).
[196] Sinkinson: Ind. Eng. Chem., **17**, 30 (1925).
[197] Thénard: Compt. rend., **78**, 219 (1874).

[198] Thiele: Z. angew. Chem., **22**, 2472-84 (1909).

[199] Tiede and Jenisch: Brennstoff Chem., **2**, 5-8 (1921).

[200] Vogel: "Handbuch für Acetylene in Technischer und Wissenschaftlichen Hinsicht" (1904).

[201] Volmar and Hirtz: Bull., (4) **49**, 684 (1931).

[202] Walker: J. Phys. Chem., **31**, 970 (1927).

[203] Wislicenus and Schmidt: Ann., **313**, 220 (1900).

[204] Wohl: Z. angew. Chem., **35**, 593 (1922); Brit. 146,258, June 28, 1920; Brit. 145,597, Aug. 4, 1921; Brit. 157,058, Sept. 1, 1921; Ger. 352,838-9, May 5, 1922; Ger. 385,708, Nov. 27. 1923; addition to Ger. 352,838.

[205] Ylla-Conte: Brit. 299,425, Oct. 26, 1927.

[206] Ylla-Conte: Brit. 301,325, Jan. 23, 1929.

[207] Ylla-Conte: Swiss, 143,697, Oct. 23, 1928.

[208] Ylla-Conte: Fr. 662,896, Oct. 25. 1928.

[209] Ylla-Conte: J. Inst. Petroleum Tech.. **15**, 744 (1929).

[210] Wheeler, McAulay and Francis: Brit. 342,319, Aug. 21, 1929; Brit. 342,359, Aug. 21, 1929.

[211] Wislicenus and Schmidt: Ann., **313**, 220 (1900).

[212] Zelinsky: Compt. rend., **177**, 882-5 (1923).

[213] Zelinsky (in part with Kasansky): Ber., **57**, 264-76 (1924).

Universal Oil Products Company,
Research Laboratories,
Chicago, Illinois.

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. IV*

BY WILDER D. BANCROFT, ROBERT S. GUTSELL,** AND JOHN E. RUTZLER, JR.***

More than thirty-two years ago MacLeod found that morphinism could be cured by the use of bromides,[1] still practical advantage has not been taken of this discovery. The fact that MacLeod's work made no useful impression seems to be due to the utter lack of understanding of why sodium bromide should help drug addicts. In the light of the theory of reversible agglomeration intelligent use can be made of MacLeod's facts. The natural attack upon the problem, bearing in mind the work with sodium bromide and the theory of reversible agglomeration, is to attempt to cure drug addiction by the use of sodium rhodanate which is a better peptizing agent than sodium bromide. Since no drug addicts were available who cared to undergo a purely experimental treatment, and since the general medical profession is loath to act upon a theory, it became necessary to perform experiments on addicted dogs.

Tatum, Seevers, and Collins[2] say: "An experimental study of morphine poisoning, both acute and chronic, has for its goal the elucidation of the corresponding conditions in man. A direct study of morphine poisoning in man is complicated by the state of mind of the subject, consequently that aspect of the problem approachable by the methods of the physiological laboratory is more safely based on controlled laboratory experimentation." So, it would seem that in some respects it was well that our first experiments were made on dogs.

Plant and Pierce[3] say that there is quite a bit of variability in the withdrawal symptoms when a group of dogs is withdrawn from morphine abruptly. The withdrawal symptoms of the dogs as a group gave a composite picture which is similar to that obtained in man. These writers conclude that the dog is the best laboratory animal for the study of morphine addiction. Tatum, Seevers, and Collins believe that the monkey is more suitable for such studies than the dog. The dog was used in our work because they are easier to obtain, less expensive, and more hardy.

Since dogs cannot administer morphine to themselves, the only way to test the validity of the theory that reversible agglomeration is responsible for many, if not all, of the symptoms of drug addiction and withdrawal is to withdraw the animals abruptly under the influence of a peptizing agent. Mental rehabilitation can hardly be studied to advantage with dogs.

[1] Bancroft and Rutzler: Proc. Nat. Acad. Sci., **17**, 186 (1931).

[2] J. Pharm. Exp. Ther., **36**, 447 (1929).

[3] J. Pharm. Exp. Ther., **33**, 329 (1928).

With the work of the above five authors as a guide, the experiments reported in this paper were made in order to determine whether or not sodium rhodanate will control the symptoms produced by the abrupt withdrawal of morphine from addicted tissues.

Six dogs were used in this work. Before the experiments were started the animals were allowed to become acclimatized to their new surroundings. This procedure eliminates such things as depression due to homesickness and physiological upsets due to change of food and habits. This collection of dogs included one male collie, designation C_1, about two years old, one female collie, designation C_2, about two years old; one female mixed hound, designation H_1, about one year old; and three female beagles, designations B_1, B_2, and B_3. The beagles were litter-mates, and were about two and one-half months of age. During the period of acclimatization the dogs were studied so that some of their peculiarities could be observed and used for comparison later on. C_1 was a wild, brainless dog; he was neither malicious nor interested in human beings. Affection did not seem to appeal to him. When chained up outside, this dog would bark continuously at the sky for long periods at a time. C_2 was a thoroughbred; she was very quiet and ladylike, with a tendency to be shy. She was not cowardly, and responded gratefully to human company. H_1 was vivacious, and continually sought human affection. B_1, B_2, and B_3 were typical puppies; they were full of life and interested in everything. They banded together when allowed outside. None of these animals showed any tendency whatsoever to be mean; although it was not easy to impress things upon C_1.

Others who have experimented on morphine addiction in dogs used large doses of morphine (30 mg. per kg. to more than 100 mg. per kg.). The smallest dosage used by Plant and Pierce was 30 mg. per kilogram; this corresponds to about 32 grains a day for an average-sized man, and is a large dose. They say, p. 342, that "there was no distinct relationship between the size of the dose at withdrawal and the severity of the symptoms although the two animals that showed very marked symptoms were withdrawn at a low dosage level (30 and 40 mgm. per kilogram)." It will be clear, in the light of the theory which will be discussed later, that any continued dosage of morphine sufficient to produce a physiological effect will bring about addiction to the drug. So, in addicting our dogs, small doses of morphine were administered at the start and the dosage level was never increased greatly. The dosage increase per unit of time in the case of C_2, B_1, B_2, and B_3 was the same, 0.0032 gram every other day from the 12th to the 41st day. The mode of addiction of these four dogs was therefore identical, disregarding variations in weight. In this manner it was hoped that the dogs could be addicted without profoundly disturbing their physiological processes. Likewise inherent physiological weaknesses should not play such an important rôle in the behavior of the animals on small doses of morphine as on large doses. Therefore the initial amount of morphine used was carefully made small enough so that the dogs were not deeply narcotized by the drug. The dosage was never increased rapidly enough to bring about narcosis.

"Abstinence[1] phenomena are more marked after a progressive rise in dosage than on a constant small or moderate dosage." It is a well-known fact that the morphinist requires more and more of the drug to "keep him comfortable" as the time during which he is addicted becomes longer. This fact is easily explained on the basis of the theory of reversible agglomeration. This corresponds to the well-known cases[2] in which more of a salt is necessary to cause agglomeration if the salt is added slowly to the sol. So, for both practical and theoretical reasons the dogs were given increasing doses of

FIG. I
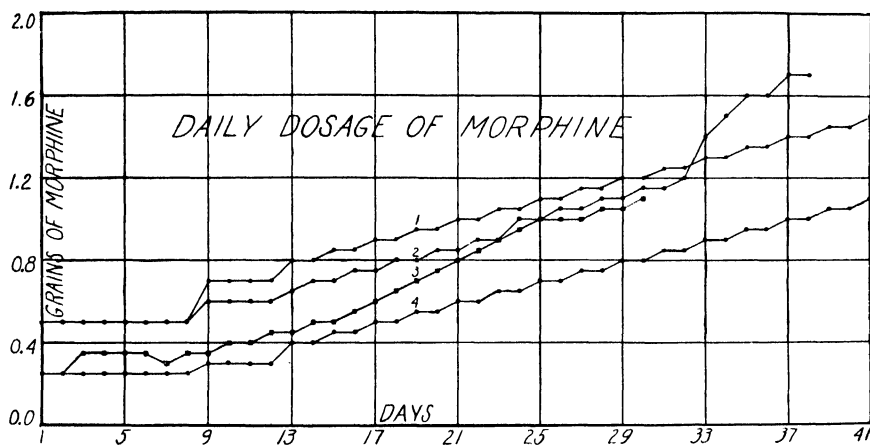
Curve 1, dog C2   Curve 3, dog H1
Curve 2, dog C1   Curve 4, dogs B1, B2, B3

morphine during this study. Fig. 1 shows the amount of morphine injected subcutaneously each day during the course of these experiments. A detailed record of the behavior of the dogs during addiction and withdrawal follows. This is useful because it shows a complete behavior picture which includes many mental reactions not hitherto described.

First Day

The addiction period was initiated on Wednesday, September 16, 1931. B1, B2, and B3 were given one quarter of a grain of morphine sulphate each at 10:15 a. m. The alkaloid was dissolved in sterile distilled water, a procedure which was followed throughout. In less than ten minutes the three dogs quieted down markedly; and each of them vomited. They did not seem to be in great distress; the vomiting was not severe. The two collies, C1 and C2 were given one half grain of morphine apiece. These dogs quieted down and vomited just as the puppies did. All of the dogs were quiet and sleepy during the afternoon; they refused food at night.

Second Day, September 17th

The dogs were injected at 9:30 a. m. They refused food at the morning feeding hour. Each of the dogs appeared to know that something was going

[1] Tatum, Seevers, and Collins: J. Pharm. Exp. Ther., 36, 452 (1929).
[2] Bancroft: "Applied Colloid Chemistry," 296 (1926).

to happen to them when the experimenters appeared. The animals became markedly quieted after the injections; all of them vomited. The effects of the morphine seemed to be manifested more quickly than on the first morning. The dogs did not appear to be so lethargic this afternoon as during the first afternoon. Their appetites were better at night.

Third Day, September 18th

The dogs accepted food this morning; they were very lively before the injections which were made at 10 a. m. This provoked vomiting within a very few minutes. All of the dogs except C_2 again were depressed by the morphine. Since C_2 was naturally quiet and well behaved, the depressing effect of the morphine was not so noticeable. Before noon the dogs were very quiet. C_1, the hyperexcitable collie who always before had barked at automobiles, did not even move when an automobile drew up. During the afternoon the dogs slept as much as they did on the afternoon of the second day. Their appetites were somewhat improved.

Fourth Day, September 19th

The injections were made at 10:15 a. m. Vomiting resulted as usual; all of the animals quieted down after the injections. The hind legs of B_1, B_2, and B_3 moved with an ataxic gait. According to Sollmann[1] this ataxia is not an unusual reaction of dogs to morphine. The animals refused their evening meal; in general they acted the same as during the third day.

Fifth Day, September 20th

The dogs were injected at 10:30 a. m. Before the injections were made, a study of the dogs showed them not to be so lively as they have been in the mornings. This may be due to the fact that it was a damp rainy day. It seemed to require a longer time for the morphine to bring about vomiting this morning. The drug quieted the dogs, as usual. The dogs are fed at 6 a. m. and 6 p. m. They have been refusing the evening meal and accepting the morning meal. The animals were more or less somnolent all day. For the last two days C_1 has been salivating a great deal. C_2 salivated after vomiting today.

Sixth Day, September 21st

Before the injections this morning all of the dogs were more animated than on the fifth day. The dogs were weighed for the first time today. Fig. 2, which will be discussed at different places in this paper, shows how the weights of the dogs varied during the course of the experiment. Morphine was injected at 10:05 a. m. today. The animals did not seem to quiet down so much after the injections today; but they all vomited as usual. C_1 salivated profusely when observed during the afternoon. He was very "dopey," and his gait was distinctly ataxic. C_2 salivated slightly, and was very quiet. B_1, B_2, and B_3 were salivated, and hardly depressed at all. By and large, the dogs were affected less by the morphine today than on other days. The dogs' appetites continued to be poor.

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[1] "A Manual of Pharmacology," 219 (1917).
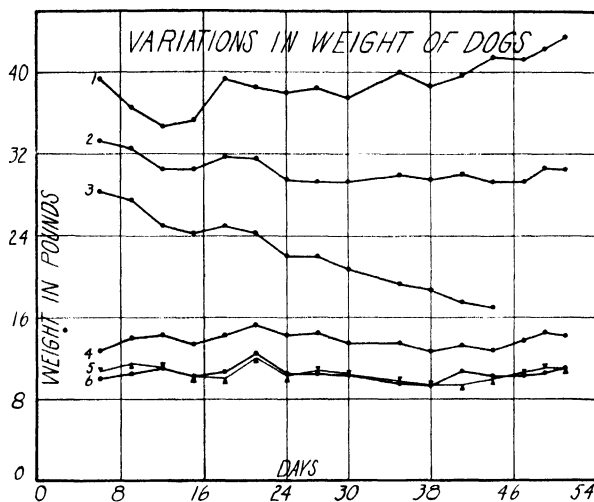
FIG. 2

Curve 1, dog C1   Curve 4, dog B1
Curve 2, dog C2   Curve 5, dog B2
Curve 3, dog H1   Curve 6, dog B3

Seventh Day, September 22nd

B1, B2, and B3 were quite active this morning, as usual. C2 was quiet, but was interested in the events occurring around her. C1 was disinterested this morning. The addiction period of H1 was started this morning. The onset of vomiting after the administration of morphine was somewhat delayed today. C1, C2, and H1 vomited; while B1, B2, and B3 were not observed to vomit at all. H1 was not depressed much by the morphine. The drug definitely did not quiet down B1, B2, and B3 so much as it had heretofore. It can be seen from the behavior of the dogs as a group that they have acquired a tolerance for morphine. During the afternoon C1 was disinterested and exhibited a very ataxic gait. This was a hot day, and C1 may be affected more by the heat than the other dogs. He went out of his way to avoid human beings. C2 was quiet, but acted much brighter than she did yesterday afternoon. B1, B2, and B3 appeared to be unaffected by the morphine that was administered during the morning. H1 was neither vivacious nor badly depressed by the morphine.

Eighth Day, September 23rd

This morning all of the dogs were much livelier than they were on the previous few mornings. C2 seemed very shy and quiet; this is probably the natural temperament of C2 for she is a bright dog, and while shy and quiet she was by no means disinterested. The dogs were unusually friendly toward the experimenters this morning. Morphine was injected at 10:35 a. m. B1, B2, B3, and C1 lost their vivacity after they were injected. No signs of vomiting were noticed. This morning it was possible to inject all of the dogs except H1 without holding them tightly. B1, B2, and B3 no longer appear to be constipated. During the afternoon C1 was more animated than he was yesterday; also, his gait was less ataxic. He appeared to be less afraid of

people than he has been. C_2 did not exhibit any depression in the afternoon from the injection. The morphine has changed the character of this dog. While she is very friendly when approached, she appears to be seclusive, quieter, and more shy than she was. She does not seem to care for human company any more; but she does not attempt to repel it. B_1, B_2, and B_3 were not excessively quiet this afternoon. Whereas they followed the experimenters around without coaxing this morning before the morphine was administered, they ran away when approached this afternoon. H_1 was quieter than during the previous afternoon; but she was not depressed much by the drug.

Ninth Day, September 24th

The dogs were quite lively this morning. C_1 appeared to both expect and want the drug. B_1, B_2, and B_3 were very salivated. C_2 was brighter today. Since tolerance to the vomiting reaction, and to a lesser degree to the depressing action, has apparently been established, the dosage of morphine was raised this morning. The dogs were weighed before they were injected. All of the dogs vomited following the injections with the exception of H_1; they were all quieted by the drug. It is interesting to note that H_1 is so constituted that her vomiting center is not stimulated by morphine like the other dogs.

When the experimenters appeared in the afternoon all of the dogs were quiet and very salivated. Upon being released, they were as animated as they were yesterday. Although H_1 was more depressed than she was yesterday she was not salivated. All of the animals whined this afternoon. The ataxia exhibited by C_1 persisted today.

Tenth Day, September 25th

The dogs acted as usual this morning; they were neither more nor less lively than on the preceding few mornings. However, they are not nearly so lively in the mornings now as they were on the first few mornings of the addiction period. Morphine solution was injected at 10:00 a. m. The dogs became quiet after the injections. H_1 vomited for the second time. All of the other dogs vomited. At noon the dogs were still quiet; they were not somnolent or greatly depressed. In general, the morphine has not caused the dogs to be "dopey" and dispirited. Their reactions are better characterized as being less vivacious and somewhat slowed down.

Eleventh Day, September 26th

All of the dogs were quite animated this morning. B_1, B_2, and B_3 began to salivate when the experimenters appeared; they were not salivated beforehand. C_2 acted quite differently today. She showed more interest in things, was much less shy, and more interested in human company. The morphine did not cause B_2 and H_1 to vomit.

Twelfth Day, September 27th

The dogs were fairly lively this morning. B_1, B_2, and B_3, and H_1 were especially lively. C_2 continues to be less shy and more interested in things. C_1 has quieted down in a most striking manner. At the beginning of the

experiment he was wild and scatter-brained. Now he is calm and does not evidence his brainless makeup so positively. Morphine was administered at 11:00 a. m. today. H_1 did not vomit and was not quieted much by the drug. C_2 vomited after the injection and then became rather quiet. C_1 vomited also. C_1 and C_2 commenced to salivate immediately after being injected.

B_1, B_2, and B_3 exhibited some interesting reactions this morning. Upon the appearance of the experimenters they all began to salivate profusely. So profuse was the salivation that the animals soon became wet all over their bodies. While B_1 was being injected, B_3 looked on and vomited before the injection of B_1 was completed. B_3 immediately consumed the vomitus showing that she was hungry and probably not nauseated. B_2 vomited so quickly after the morphine was injected that the mechanism probably was not a stimulation of the vomiting center; she consumed the vomitus also. Reach[1] considers that salivation before and after the injection of morphine is a withdrawal symptom. Pavlov[2] and Collins and Tatum[3] call it a conditioned reflex. Pavlov also describes reflex vomiting similar to that just pictured. There does not seem to be much question but that Pavlov is right; because, as will be seen later increasing the dosage of morphine failed to stop the salivation. Also, all of the dogs began to salivate when the experimenters appeared, no matter what time of day it was, or whether before or after the injections of morphine were made. It was determined definitely that visitors did not induce this reaction.

Thirteenth Day, September 28th

The dogs were just as lively this morning as they were yesterday morning. They began to salivate shortly after seeing the experimenters, with the single exception of H_1. The morphine dosage was increased today for all dogs except H_1. The injections were made at 10:00 a.m. B_1, B_2 and B_3 vomited; but the other dogs did not. The larger dosage did not cause the dogs to become more quiet than usual.

During the afternoon the animals acted no differently, so far as general appearance goes, than they did on the smaller dosage. They were not particularly quiet. C_2 was shy and self-contained, thus reverting to her earlier condition. B_1, B_2, B_3 and C_1 salivated profusely when the experimenters came in sight. The dogs' appetites are better than they have been so far during the experiment.

Fourteenth Day, September 29th

C_2 was less shy again today. When one of the experimenters came into the cage she prostrated herself at his feet. C_1 is becoming quieter and quieter. H_1 still acts very animated in the morning. B_1, B_2, and B_3 have quieted down in the last few days so that they are not nearly so animated in the morning as they were during the first week of addiction. B_1, B_2, B_3 and C_1 salivated profusely when the experimenters appeared. Morphine was ad-

[1] Z. exp. Path. Therap., 16, 321 (1914).
[2] "Conditioned Reflexes," 35 (1927).
[3] Am. J. Physiol., 74, 14 (1925).

ministered at 10:00 a.m. C_1, B_2, and B_1 vomited within 15 minutes after the injections. To date H_1 has been comparatively refractory to the drug; for it has not affected her as much as the other dogs.

Fifteenth Day, September 30th

Profuse salivation commenced today when the experimenters appeared. C_2 exhibited a different reaction again today. The cloak of shyness has fallen once more; and she was more investigative. For the past few days this dog has submitted to the injection very undemonstratively. She appears to be ready for it when the experimenters approach her. H_1 was vivacious this morning. C_1 walked up to the experimenters as though he desired to be injected. When one of the beagles was taken out of the cage and into a room to be weighed and injected, the two other beagles began to howl. All of the dogs submit to the injections quietly so that extremely little restraint is necessary during the manipulation. The injections were made at 10:15 a.m. Each of the dogs was examined for tenderness in the regions where the injections have been given. Since no tenderness was found, the conclusion is drawn that the dogs are not suffering from abscesses.

No vomiting was witnessed after the morphine was administered today. Also, there was little, if any depression produced by the drug. To date the dogs have been on a diet of bread and milk.

Sixteenth Day, October 1st

The dogs presented the same general behavior picture this morning as they have for the last two mornings. The dogs salivated profusely, as usual. Morphine was administered at 10:30 a.m. B_2 was taken out of her cage and into a room to be injected. The other two dogs, B_1 and B_3, howled almost as soon as the room door was closed. The morphine had very little affect on H_1; she did not vomit or become depressed. C_1 and C_2 did not vomit. B_1, B_2, and B_3 did vomit.

C_1, C_2, and H_1 were fed a pound of raw hamburg each; B_1, B_2, and B_3 were each given one-half pound of the raw meat at the evening meal time. C_2 refused to eat hers at the time, but ate it during the night.

Seventeenth Day, October 2nd

B_1, B_2, and B_3 were considerably more animated today; C_2, H_1, and C_1 acted as they have for the last few mornings. None of the dogs appears to be constipated. All of the dogs, except H_1, salivated when the experimenters appeared. Morphine was administered at 10:30 a.m. The drug did not have any quieting effect on any of the dogs, with the exception of H_1. She became only slightly less lively.

About ten minutes after being injected C_1 began to whine and bark. He was not barking at anything in particular; he turned his head away from the experimenters when he barked. The bark was a peculiar explosive half-hearted yelp. So far as could be determined there was no external cause for pain. This description of the behavior of C_1 illustrates the psychiatric abnormality of the dog which will be considered in detail later.

The dogs were not seen vomiting today. At no time, before or after this day, during the experiment have any of the dogs growled, snapped, or acted mean in any way either during, before, or after the injections.

During the afternoon H_1 was quiet and retiring. The other dogs acted the same as they have for the last few mornings before being given morphine. C_1, C_2, and H_1 were each given a pound of raw hamburg. H_1 and C_2 refused to eat the meat. C_2 made vomiting movements when the meat was presented; she consumed the meat during the night. H_1 did not eat the meat at all. C_1 ate the meat hungrily; he was extraordinarily quiet and gentlemanly in the way he took the meat. B_1 and B_3 were given three-quarters of a pound of meat. B_2 refused the meat.

Eighteenth Day, October 3rd

With the exception of H_1, all of the dogs were livelier this morning than they have been during the past week. They all salivated prior to the administration of the drug; this is the first time that H_1 has salivated. The injections of morphine were made at 10:00 a.m. B_1, B_2 and B_3 were taken, one at a time, into the weighing room to be given the hypodermic. When B_1 was taken into the room, B_2 and B_3 began to howl. B_3 began to howl when B_2 was taken into the room. This reaction on the part of the dogs left behind being repeated, as it has, signifies either one of two things; either they wanted the injection of morphine, or they did not want their sister dog taken away from them. In the light of the behavior of the dogs later in the experiment, the former reaction seems to be the more likely.

None of the dogs vomited after their dosage of morphine; likewise they were quieted very little by the drug. Of course, the dogs are not now so animated before the drug is injected as they were during the earlier part of the experiment. C_1 was more excitable this morning, and would not stand still while being injected. On the whole, the dogs seem very lively for the amount of morphine that must be in them.

Nineteenth Day, October 4th

Again this morning the dogs seemed a little more lively than they have been for the past week. The experimenters drove up to, and then 30 yards past the door of the experimental barn, and stayed there for about ten minutes. In a few minutes the dogs in the barn began to bark and howl. The loud baying of B_1, B_2, and B_3 could be distinguished clearly. Upon entering the experiment station none of the addicted dogs barked; whereas three other dogs continued to make a disturbance. C_1 was profusely salivated at this time. B_1, B_2, B_3, C_2, and H_1 commenced to salivate upon seeing the experimenters. C_1 balked at being injected today, as he did yesterday. The drug did not quiet the dogs, with the exception of H_1. She did not show much effect from the injection.

Each of the three beagles was given its morphine just outside of the cage in the sight of the others. While B_1 was being injected B_2 and B_3 bayed loudly. Likewise B_3 bayed while B_2 was being injected. These dogs now stand still

without being restrained at all while being given the hypodermic; they wag their tails during the process. C_2 and H_1 do not have to be held either. All of the dogs were fed Calo dog food at night. With the exception of H_1 they ate well.

Twentieth Day, October 5th

The process of driving past the door of the experiment station was repeated today with the same result as yesterday. The addicted dogs apparently become restless during the middle of the morning before they are given morphine. The restlessness subsides when the drug is given. The hypodermics were given at 11:00 a.m. Prior to this all of the dogs salivated. The morphine did not provoke vomiting.

B_1, B_2, and B_3 repeated their baying performance of yesterday. The drug no longer seems to quiet the dogs after the injections.

Twenty-first Day, October 6th

The dogs did not make a commotion when the experimenters arrived today. Morphine was administered at 11:00 a.m. All of the dogs were salivated this morning. B_1, B_2, and B_3 repeated their act of the last two days. With the exception of C_1, all of the animals stand still without being held while the injections are made. There were no evidences of vomiting after the morphine was administered today. C_1 is somewhat rebellious while being injected; his high degree of excitability is maintained. C_2, C_1, and H_1 appear to be constipated.

Twenty-second Day, October 7th

Again today the dogs did not make a commotion when the experimenters waited outside of the experiment station. All of the dogs salivated profusely before being injected; B_1, B_2, and B_3 were quite a good deal more salivated than the other dogs. This has been the case ever since these three dogs began to salivate. Morphine was administered at 10:15 a.m. The three puppies did not repeat the baying act.

None of the dogs vomited after being given morphine. C_2 was somewhat less shy this morning; she was bothered by diarrhea. C_1 had diarrhea also.

Twenty-third Day, October 8th

Another interesting reaction was observed this morning. The day was dark and wet; and all of the experimental dogs were noticeably more quiet than usual. Three other dogs at the experiment station acted no differently than on other days. This same reaction has been observed several times. Quite independently of this the authors have been told by addicts who are not using the drug, but whose nervous systems have not returned to normal, that on dark, damp days they feel depressed. So, there seems to be an analogy here between the behavior of man and dogs.

Morphine was administered at 10:30 a.m. B_1 and C_1 both vomited after the drug was given. The reaction was not so severe as usual. C_1 did not struggle while being injected. His hyperexcitability has disappeared. Neither

C_1 nor C_2 was bothered by diarrhea today. B_1, B_2, and B_3 are not constipated. Most of the animals now wag their tails while being injected.

Twenty-fourth Day, October 9th

It was cold today, and the addicted dogs were quiet. The other dogs were noisy. All of the experimental dogs began to salivate profusely before being injected. The drug was administered at 10:30 a.m. Only C_1 had to be held while this was done. None of the dogs came of their own accord into the room where the injections were made. C_1 and B_1 vomited after being given the morphine. No signs of diarrhea were seen. C_2 was less shy than she has been.

When the experimenters appeared in the afternoon all of the dogs began to salivate. There were other persons observing the animals when the experimenters came; but they did not cause the dogs to salivate. The degree of salivation was not nearly so great as it is in the morning before the dogs are given morphine.

The dogs were fed Ken-L Ration during the afternoon. C_1, B_1, B_2, and B_3 consumed it voraciously; the latter three dogs pranced around and fought for it. Yet the dogs refuse bread and milk, which they formerly liked. C_2 ate the Ken-L Ration in a very lady-like manner. The experimental dogs have refused all but very appetizing food for the last two weeks.

Twenty-fifth Day, October 10th

All of the dogs salivated profusely this morning, when the experimenters appeared. While the animals were being observed, and before any preparations whatever were made for the injections, C_1 and B_1 vomited. This was in all probability reflex vomiting. Morphine was administered at 10:00 a.m. None of the dogs vomited after the injections. They were fed Ken-L Ration during the afternoon.

Twenty-sixth Day, October 11th

The experimenters arrived late in the morning. Despite the cold wet day, there was a great deal of barking and excitement. Upon entering the experiment station the addicted dogs became quiet, and showed no signs of excitement. The dogs salivated as usual. H_1 was bothered by diarrhea. None of the animals vomited after the morphine was administered at 12:30 p.m.

Twenty-seventh Day, October 12th

The dogs began to salivate soon after the experimenters arrived. Morphine was injected at 10:15 a.m. It has been noticed that a short time after the drug is given the dogs stop salivating. C_1 was restless and hyperexcitable while being injected. He protested physically, but did not growl or snap. The other dogs did not have to be held while being injected. None of the animals vomited after being injected; further, they were livelier than usual after the drug was exhibited.

Twenty-eighth Day, October 13th

When the experimenters arrived the dogs salivated, as usual. C_1 is almost as scatter-brained and crazy as he was before the experiment was started.

Morphine was administered at 9:15 a.m. C_1 again protested against being injected. He vomited shortly after the injection. This was probably reflex vomiting for he consumed the regurgitated material. None of the other dogs vomited.

Twenty-ninth Day, October 14th

In order to observe the reactions of the dogs if the exhibition of morphine were delayed, the animals were not injected until 5:30 p.m. After mid-morning the addicted dogs were markedly uneasy and barked almost continuously until the experimenters came to inject them. The dogs became quiet and began to salivate when we arrived. C_2 did not salivate until the injection was started. B_1, B_2, and B_3 were slightly restless and wandered around their cage in an aimless manner. None of the dogs vomited after having morphine. C_1 did not protest nearly so much as he did yesterday when given the drug. So it can be assumed that the dogs now have a physical need for morphine.

At times several of the dogs have been bothered by conjunctivitis.

Thirtieth Day, October 15th

All of the dogs were salivated before they were given morphine. The drug was administered at 10:15 a.m. The animals did not vomit after being injected. The morphine quieted the dogs more than usual today; this is probably due to the fact that a shorter time than usual elapsed between the last two injections. The conjunctivitis noticed in H_1 and C_2 was treated with argyrol.

C_1 protested strongly against the injection this morning. For the past week it has been noticed that the dogs attempt to defecate shortly after morphine is administered.

Thirty-first Day, October 16th

Each of the addicted dogs began to salivate when observed by the experimenters. C_1 remains scatter-brained and senseless; he protested against being injected. The dogs were quieted by the morphine somewhat more than usual. None of the animals vomited after morphine was exhibited. The conjunctival condition of C_2 and H_1 is better today; it was treated again with argyrol.

Thirty-second Day, October 17th

Despite the fact that it was a cold and rainy day, the dogs were a little more lively; all salivated prior to receiving the drug. Morphine was injected at 10:00 a.m. B_1, B_2, and B_3 wagged their tails while being injected. This has occurred for several days. It was definitely determined that the animals wag their tails much harder *while the solution is running out of the needle*. The phenomenon commences during the pre-injection handling of the dogs; they do not wag their tails harder when the needle is thrust under the skin.

H_1 and C_2 are no longer suffering from conjunctivitis.

C_1 presents a strange figure; during the injection he acted in a weird, scatter-brained manner. Then he vomited. Following this, for the second time in the last two days, he stood motionless with his head in a corner of the

cage for quite a while. Further, during the last few days he has gnawed a two by four inch timber almost half in two. Plant and Pierce[1] consider this to be a withdrawal symptom. Therefore the dosage of morphine was raised more rapidly from this day on.

The dogs were depressed extremely little by the morphine today.

Thirty-third Day, October 18th

The dogs began to salivate as usual this morning upon the appearance of the experimenters. Morphine solution was injected at 11:00 a.m. C_1 protested wildly against the injection; in doing so he was not either mean or ugly in any way. He vomited after being given the morphine. B_1, B_2, and B_3 repeated their tail wagging episode. C_1 has a maniacal look.

The dogs were fed Ken-L Ration during the afternoon. C_1, B_1, B_2, and B_3 took this food voraciously. C_2 refused to accept the food while being observed or coaxed. As soon as the experimenters were out of sight, she ate heartily. H_1 refused food entirely. A neutral, uninstructed observer remarked casually that C_1 looks like a maniac; it should be stressed that this dog has never cared for human society since coming to the experiment station. This afternoon it was again demonstrated that only the experimenters elicit the salivation reaction. A stranger watched the dogs for five minutes, and saw no salivation. Yet, a minute or two after the approach of one of the experimenters the dogs began to salivate. The secretion was not so profuse as it has been on other afternoons.

All of the addicted dogs have undergone a change of character. They slink and act as though they have done something wrong, when they are approached.

Thirty-fourth Day, October 19th

H_1 and C_2 failed to salivate when the experimenters watched them. C_1 was somewhat more quiet this morning. Morphine was administered at 10:30 a.m. C_2 vomited severely after the injection. H_1, B_1, B_2, and B_3 *began to wag their tails only when the morphine solution began to run through the hypodermic needle.* All of the dogs except H_1 seemed hungry when fed Ken-L Ration.

C_1 balked at being injected so strongly that it was not advisable to try to administer the morphine while he was being held tightly. The dog quieted down when he was soothed, stroked, and talked to; this was continued, and he submitted to the injection without protesting. It was not necessary to restrain him at all.

Thirty-fifth Day, October 20th

With the exception of H_1, the dogs salivated when the experimenters appeared. She did not salivate either before or after the injection. She has conjunctivitis again; it was treated with argyrol. As has been the rule for the past couple of weeks the dogs were quiet before morphine was administered. C_2 was difficult to inject again this morning; he stopped making a fuss when he was soothed.

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[1] J. Pharmacol. Proc., **31**, 210 (1927); J. Pharm. Exp. Therap., **33**, 343 (1928).

None of the animals vomited after being given morphine. H_1 and C_2 became much more quiet after the drug was given. H_1 and B_2 wagged their tails when the liquid ran out of the hypodermic needle.

Thirty-sixth Day, October 21st

There were no unusual occurrences today except the following. C_2 vomited after being injected. H_1 and C_2 were treated with argyrol for conjunctivitis. H_1 was not salivated. C_1 was difficult to inject. All of the dogs except C_1, wag their tails when the morphine solution flows from the needle.

Thirty-seventh Day, October 22nd

Morphine was not administered until 6:00 p.m. The dogs were noisy all afternoon. They were quiet when the experimenters arrived. They became noisy when the experimenters did not enter the barn. It was obvious that the dogs were distinctly more friendly to the experimenters than they usually are. H_1 and C_2, in particular, came up to us in an extremely friendly manner. C_1 began to salivate before he saw the experimenters. H_1 did not salivate at all. C_1 was not quite so difficult to inject as he has been in the last few days. None of the dogs vomited after morphine was administered.

It was decided that the dogs show sufficiently definite signs of addiction to morphine for them to be prepared for withdrawal. Accordingly C_2 and B_3 were selected for abrupt withdrawal without sodium rhodanate. The other dogs with the exception of C_1 are to receive daily doses of sodium rhodanate for a period of four days prior to abrupt withdrawal. During this time morphine will be continued in increasing doses. C_1 will be given sodium rhodanate today and be withdrawn abruptly tomorrow. C_1 was given 0.4 grams of sodium rhodanate in a gelatine capsule buried in a small ball of meat. B_1 and B_2 were given one capsule each containing 0.2 gram of sodium rhodanate in a similar manner. A capsule containing 0.2 gram of sodium rhodanate was forced down the throat of H_1. Sodium rhodanate was followed in ten or fifteen minutes by the injection of morphine. The dogs that were given sodium rhodanate seemed to become more quiet than the others after morphine was administered.

Thirty-eighth Day, October 23rd

When observed this morning C_2 and B_3 did not seem to be quite as bright as the other dogs. All of the dogs except H_1 began to salivate when the experimenters appeared. C_1 objected strenuously to being injected. Since raising the dosage of morphine more rapidly, this dog has not stopped gnawing the timbers of his cage. It seems therefore that gnawing is not necessarily a withdrawal symptom. In this case it is considered to be a nervousness which parallels his general peculiar character changes. The injections were made at 10:30 a.m., dosage with morphine being continued. B_1, B_2, and B_3 were not given morphine first this morning; they whined while the other dogs were being injected. H_1 made vomiting motions after the drug was given.

Sodium rhodanate was given again this morning. The doses administered were: H_1, 0.2 gram in a capsule per os, C_1, 0.4 gram in a capsule in meat per os, B_1, 0.2 gram in a capsule in meat per os, B_2, 0.2 gram in water by subcutaneous injection.

Thirty-ninth Day, October 24th

All of the dogs salivated when the experimenters appeared, except H_1. The dogs were quiet as has been usual in the morning for the past few weeks. C_1 did not look so maniacal today. Morphine was injected at 10:15 a.m., none of the dogs vomited afterward. C_1 was withdrawn abruptly today, that is he received no morphine.

Sodium rhodanate was administered again today. C_1 was given 0.4 gram in a capsule in meat per os. H_1, B_1, and B_2 were given 0.2 gram each in water solution by subcutaneous injection. The injection was quite painful to B_1, it did not pain B_2 or H_1.

Fortieth Day, October 25th

C_2 salivated more profusely than ever today; H_1 did not salivate at all, and B_2 salivated very little. For the last few days B_2 has not salivated much. This dog acts more nearly normal than she has for some time. Morphine was administered at 11:00 a.m. None of the dogs vomited after the injections.

The behavior of C_1 deserves special mention. He looks definitely less maniacal than he has lately. This morning he was more friendly than he has been for three or four weeks. He did not act so brainless and crazy as he has during the entire course of the experiment. He was lively in a normal way, which is most unusual. These changes were sharp and well-defined. He still gnaws at the supports of his cage. He passed a soft stool today.

Sodium rhodanate was administered as follows: C_1, 0.6 gram in a capsule in meat per os; H_1, B_1, and B_2, 0.2 gram in water solution by subcutaneous injection. These injections did not pain any of the dogs today.

Forty-first Day, October 26th

Morphine was administered at 3:30 p.m. The dosages of sodium rhodanate given were: C_1, 0.4 gram in a capsule per os in meat; H_1, and B_2, 0.2 gram in water solution by subcutaneous injection; B_1, 0.3 gram in water solution by subcutaneous injection.

C_1 continues to gnaw industriously at the wood supports of his cage. For the first time in many weeks he showed interest in another dog. He does not show signs of diarrhea. The dog salivated less than usual. He showed definite signs of interest in human affection; he sought stroking by the experimenters. When led from place to place he did not balk as he does usually. A rapid, nervous opening and shutting of the jaws was noticed. The action did not last long, and was probably an effort to free his mouth and lips of saliva. This animal is improved much today; remarkable improvement in his general behaviour has been noticed in the last few days.

H_1 is in very poor physical condition; she is, and has been, losing weight rapidly. She did not salivate today. Her nose is stopped up by dried mucus; the nasal passages are very dry. The conjunctivitis has disappeared. The injection of sodium rhodanate did not appear to pain her. This dog and B_3 have been and are more interested in other dogs than are any of the experimental animals. H_1 sprawled out on the floor of her cage and gave the appearance of being drowsy after the injections. She is markedly tender over the hips.

C_2 salivated today, as usual. For the last few days she has turned over on her back when the experimenters came to her cage. This may be an indication that she wants the drug. The condition of this dog remains the same as it has been.

B_3 now is the liveliest by far of the three litter-mates, B_1, B_2, and B_3. When Ken-L Ration was offered to these three dogs only B_3 showed any interest in it; she consumed it all. She wagged her tail when the morphine solution ran out of the needle.

B_1 exhibited a reaction of pain to the injection of sodium rhodanate today. After the injections she curled up in her cage and was disinterested.

B_2 seems to be disturbed by the treatment. She was disinterested when the experimenters arrived, and remained so after the injections. She has not been so salivated as the other dogs, of late; today she began to salivate quite a little while after B_1, and B_3 began. The injection of sodium rhodanate did not cause this dog or H_1 to be in any pain. B_2 vomited often yesterday; she shivered, and was not lively.

When sodium rhodanate is injected the dogs do not wag their tails; whereas they do wag them when morphine is injected.

This is the last day that morphine will be administered to any of the dogs. Abrupt withdrawal will begin, therefore, tomorrow.

Forty-second Day, October 27th

Sodium rhodanate was administered at 12:00 noon as follows: C_1, 0.4 gram in a capsule in meat per os; H_1, B_1, and B_2, 0.2 gram in water solution by subcutaneous injection.

H_1 did not salivate when the experimenters approached. This dog is a sick dog, and has been that way for a week. The rapid loss of weight has weakened her considerably. She was not well before sodium rhodanate first was administered. During last night she stretched out on her side and was extremely disinterested. She was better this morning; she was more friendly than she has been for a couple of weeks. Her eyes were very pussy today; the condition was treated with argyrol.

C_1 was more friendly again today. He is more quiet than he has been for some time; this does not appear to be due to depression. He is merely acting more like a normal dog. His stools are soft; but he does not have diarrhea. His appetite is good. He does not salivate so much as he did; most of the time his ears are pricked up and he is alert.

B2 appeared to be subdued and disinterested; there was no change in her response to human affection, that being strong as usual. This dog did not salivate when the experimenters were around. The injection of sodium rhodanate evidently caused no pain.

B1 was salivated profusely when the experimenters appeared. The injection of sodium rhodanate did not hurt this dog so much today. She did not become disinterested after the injection.

C2 salivated as usual when the experimenters observed her. B3 acted likewise. These two dogs showed no change in condition.

Forty-third Day, October 28th

Sodium rhodanate was administered as follows: C1, 0.4 gram in a capsule in meat per os; B1 and B2, 0.2 gram in water solution by subcutaneous injection. H1 was not given any sodium rhodanate on account of her poor physical condition. This dog has distemper; that is what has been ailing her. Other than to say that H1 did not at any time show withdrawal symptoms, the detailed account of her behavior from this time on will be omitted.

C1 continues to improve; he is a sensible dog now. He has ceased gnawing at the wood in his cage. The dog was only slightly salivated today; and there are indications of diarrhea. Other observers have noticed that this animal is brighter. His appetite is better.

C2 passed soft stools today. Only a very careful study revealed her true condition. The dog appears to be much brighter with not such a far-off look in her eyes. Upon the arrival of the experimenters she entirely forsook her shyness and quiet demeanor and approached them tail wagging, head up, with no hesitation, and without being called. This behavior was so foreign to her general conduct that her actions were like those of a different dog. This performance was repeated; she was then shown the hypodermic syringe which she nosed in a thoughtful manner. When the motions of injecting her were made she wagged her tail much harder. The dog quite definitely wanted the injection. Upon approaching the dog without the syringe in hand, she did not stir out of her corner. This was repeated several times with the same result. This dog either thought that the needle being thrust under the skin was an injection of morphine, or that by being friends she would not be given morphine. If the former situation is the correct one, there is in the actions of this dog a distinct parallel to the behavior of human addicts. On the other hand she may have learned quickly that she was not to have morphine today. The brightness and friendliness exhibited by this dog were probably due to nervousness. A slight horizontal head tremor was noticed.

B3 exhibited the same head tremor as C2; otherwise there was no change in her condition.

B2 was more lively than she was yesterday; she did not salivate when the experimenters appeared. There was no change in the condition of B1.

Forty-fourth Day, October 29th

H1, B1, and B3 were each given 0.2 gram of sodium rhodanate dissolved in water by subcutaneous injection at 12:00 noon. C1 was not given sodium rhodanate.

All of the dogs except H1 and B2 salivated when the experimenters appeared. None of the dogs salivated so profusely as they have been doing.

C2 behaved in the same peculiar manner that she did yesterday. The head tremor persists. The dog passes stools frequently. She refused Ken-L Ration.

B3 defecates often. She is definitely nervous; a slight head tremor is noticed now and then. Today she was not so friendly as B1 and B2 were. The animal would not eat Ken-L Ration. There was a very fine general body tremor that could not be detected with B1 and B2. ·

B1 and B2 were quite friendly today; but they were not unusually so, as C2 has been. They appear to be very slightly depressed. No special change was noticed today. These dogs are not passing soft stools as B3 and C2 are.

C1 was no different than he was yesterday.

Forty-fifth Day, October 30th

Sodium rhodanate was administered only to C1 today; he was given 0.6 gram in a capsule in meat per os at 5:30 p.m. C1 exhibited some important changes. He has lost all interest in human affection, is scatter-brained again, and has a maniacal look in his eye. Evidences of diarrhea were seen. The dog vomited reflexly upon seeing the experimenters; there was apparently a spastic condition of the stomach. He was hungry for he consumed the vomitus immediately. When being watched he turned his head and body toward the inside corner of the cage. This appeared to be due to negativism rather than to photophobia. The animal salivated when the experimenters appeared. He has resumed gnawing, having gnawed a hole in the wall. Shortly after being given sodium rhodanate the dog vomited again. It is important to note that this dog has not had sodium rhodanate for almost two days, which accounts for his peculiar actions. When one attempted to pat the dog he walked off. Every once in a while he emitted a low moaning whine.

C2 behaved like an entirely different dog today. When observed she was lying stretched out on her side in a disinterested fashion. Although she wagged her tail in a feeble manner, she neither moved the bulk of her body or looked up when the experimenters came. Upon entering the cage she made no movement to arise. After several repetitions of this the dog finally arose slowly. She laid down again almost immediately; and she did not move around during the brief time that she was on her feet. Although the dog was disinterested and was not lively at all, she did not in any way resent affection. The dog salivated when the experimenters came. The head tremor was pronounced today. The dog has diarrhea. She had no appetite, as was evidenced by the fact that fresh meat remained untouched in her pan.

B_3 was disinterested today; she did not move when first approached in her cage. She showed little interest in leaving the cage when given an opportunity to do so. When she wandered about the cage a little her movements were slow and aimless. She showed evidences of nervousness. Normally the hungriest of the three young dogs, she refused fresh meat; whereas B_1 and B_2 ate all that was offered them. B_3 salivated when the experimenters appeared. There was a pronounced head tremor today; and the body tremor is stronger than it was yesterday. She is doing considerable gnawing at her cage. B_1 and B_2 acted about the same as they did yesterday. The dogs seemed to be hungry for meat, particularly B_2. No soft stools were noted. The dogs arose when the experimenters entered the cage, and were friendly. They seemed more interested than they did yesterday; they cared for human affection, and did not wander aimlessly about. The general health of B_2 seems to be better than it has been since the start of the experiment. B_1 salivated when the experimenters appeared, B_2 did not.

None of the dogs salivate so profusely as they did when receiving morphine.

Forty-sixth Day, October 31st

Sodium rhodanate was administered at 10:30 a.m. in water solution by subcutaneous injection. H_1 was given 0.1 gram, and B_1 and B_2 0.25 gram each.

C_2 was inquisitive about the hypodermic syringe when it was shown to her. She wagged her tail rapidly when motions were made to inject her. She was lying on her side when first observed, and did not get up at all. She wagged her tail feebly when she first saw the experimenters. A very fine body tremor accompanied the head tremor. Her appetite seems somewhat better. The dog continues to pass many stools. She salivated when the experimenters appeared.

B_3 acted about the same as she did yesterday. She was perhaps a little more quiet today. She was neither friendly nor unfriendly. The head and body tremor were still present. She salivated when the experimenters appeared. Her appetite seems to be better.

C_1 was changed again today. He was more friendly and interested in what was going on. The maniacal look in his eye subsided; he did not face the back of his cage. So, sodium rhodanate again caused a change for the better in this dog. There were signs of diarrhea.

B_1 and B_2 were more lively today. The general health of B_2 in improving rapidly. Both dogs salivated when the experimenters appeared. No soft stools were passed by these dogs. B_1 and B_2 were extraordinarily demonstrative and friendly today. Since they were not given sodium rhodanate yesterday, this reaction may be interpreted as a desire for morphine such as was shown by C_2 on the forty-third day. In complete contrast to B_3, B_1 and B_2 were anxious to leave their cage. A test for the rhodanate ion in the saliva was positive in the case of B_1 and B_2.

Forty-seventh Day, November 1st

Sodium rhodanate was administered as follows: C_1, 0.6 gram in a capsule in meat per os; B_1 and B_2, 0.2 gram in water solution by subcutaneous injection.

All of the dogs except H_1 have had, in general, better appetites since the morphine was withdrawn, despite the fact that at times for periods of about 36 hours some of the animals refused food. Despite the better appetites C_2 and B_3 have decreased slightly in weight since withdrawal; while B_1, B_2, and C_1 have gained weight steadily. This is shown by the figures in Table I, the values being those on the last part of Fig. 2.

TABLE I

Weights of Dogs in Pounds during Withdrawal

Day	Wght. C_1	Wght. C_2	Wght. B_1	Wght. B_2	Wght. B_3	Remarks
38	38.75	29.50	12.75	9.25	9.25	C_1 withdrawn
41	39.75	30.00	13.25	9.25	10.75	C_2, B_1, B_2, B_3
44	41.50	29.25	12.75	9.90	10.25	withdrawn
47	41.25	29.25	13.75	10.50	10.25	
49	42.25	30.75	14.50	11.0	10.50	
51	43.50	30.50	14.20	11.0	11.00	

The table shows that over the whole post-withdrawal period C_1 gained weight steadily. C_2, somewhat under her original weight, did not change much. B_1 and B_2 gained slowly; while B_3 stayed about the same. The dogs that were not protected by sodium rhodanate therefore did not pick up so rapidly as those that were protected. Averaging the losses in weight of 18 dogs during the first week of withdrawal in the experiments of Plant and Pierce, we find that it was about one pound. Only one dog in 21 gained weight.

C_1 showed continued improvement today. He was friendly, showed an interest in other dogs, wanted to leave his cage, and barked continuously at nothing in particular when chained up outside. Thus, some of his actions were much the same as before he was addicted. He salivated very little when the experimenters appeared. He does not gnaw at his cage any more. There were only a few stools in the cage. The pupils of his eyes were normal.

B_3 was somewhat more lively today. The head and body tremors persist. She salivated only slightly when the experimenters appeared. Many soft stools were noted. The dog is still depressed. The pupils of her eyes were widely dilated.

C_2 was a little more lively and friendly. She did not arise when the experimenters appeared. When she did arise it was only for short periods of time after which she would resume her reclining position. He head tremor persists. This dog still shows a defect in interest. She exhibits a peculiar blowing movement whereby she blows air out with her mouth closed in such

a manner as to make her upper lip move rapidly out and in. C1 exhibited the same picture several days ago. This may be due to nervousness. The pupils of her eyes were about normal.

There was not much change in the condition of B1 and B2 today. They both salivated when the experimenters appeared. B1 salivated more than she has for several days. B2 continues to present a more healthy general appearance; there is a noticeable daily improvement in the condition of this dog. B1 and B2 apparently are passing as many stools as C2 and B3; but the stools of the former are hard while those of the latter are soft. B1 and B2 were not so demonstrative as they were yesterday; but they were neither aloof nor depressed. They were anxious to leave their cage in contrast to B3 and C2. When sodium rhodanate is injected into these dogs they do not wag their tails as they did when morphine was injected. They learned the difference between the two very quickly. The pupils of their eyes were normal.

Forty-eighth Day, November 2nd

All of the dogs except H1, salivated when the experimenters appeared. Likewise, all of them were lively. The head tremor of C2 persists. C1 yelped continuously and senselessly at the sky when put outside. B3 still exhibits the body tremor; she was interested in leaving her cage today. Sodium rhodanate was not given to any of the dogs.

Forty-ninth Day, November 3rd

The pupils of the eyes of the several dogs make an interesting study. According to Lambert[1] dilation of the pupils is a common withdrawal symptom. The pupils of the eyes of B3 were widely dilated and responded only slightly and sluggishly to light. In the case of C2 the pupils were widely dilated; but they were sensitive to light. B1 and B2 presented normal pupils. The pupils of the eyes of C1 were somewhat larger than normal.

B3 has a fine body tremor; she is not disinterested any more. C2 still exhibits a head tremor. All of the dogs began to salivate when the experimenters appeared. B1 and B2 salivated more profusely than the other dogs. They were friendly and interested today.

Sodium rhodanate was not administered.

Fiftieth Day, November 4th

B1 and B2 were quiet today. The pupils of their eyes were somewhat dilated; so they were each given 0.25 gram of sodium rhodanate in water solution by subcutaneous injection. These two dogs eat anything and everything that is given to them.

C2 did not salivate when the experimenters appeared. The other dogs did; it has been noticed that the induction period for salivation is becoming much longer. C2 was not active this morning. She has diarrhea. She is

[1] Am. J. Psychiatry, 10, 504 (1930).

not eating food well. B3 has a very poor appetite, also; a pronounced body tremor still persists.

There was no change in the condition of C2 today.

Fifty-first Day, November 5th

The appetites of B3 and C2 continue to be poor. All of the dogs except H1 were active and practically normal today. None of the dogs exhibited dilated pupils. The dogs salivated, as usual, when the experimenters arrived. The pupils of B1 and B2 were normal.

This concludes the post-withdrawal study.

Summary and Discussion

Tables II and III gather together in brief form some of the important data on this experiment.

TABLE II

Dog	Daily Morphine Dosage at Start	Daily Morphine Dosage* at Withdrawal	Weight 6 days after start	Weight at withdrawal	% Increase of Morphine Dosage
C1	1.8 mg/kg.	6.26 mg/kg.	17.8 kg.	17.55 kg.	350
C2	2.1	7.15	15.1	13.6	340
H1	1.3	9.79	12.8	7.9	750
B1	2.8	11.84	5.77	6.0	420
B2	3.3	16.9	4.87	4.2	510
B3	3.6	14.6	4.5	4.87	410

*A 150-pound man addicted to 5 grains of morphine per day would be taking a daily dose of the drug which amounts to 4.76 mg/kg.

TABLE III

Dog	Sex	Number of days on Morphine	Amount NaCNS before Withdrawal	Amount NaCNS after Withdrawal	Days NaCNS Continued after Withdrawal	Total Amount NaCNS
C1	M	38	0.8 gm.	3.4 gm.	10	4.2 gm.
C2	F	41	0.0	0.0	0	0.0
H1	F	35	1.0	0.5	5	1.5
B1	F	41	1.1	1.3	9	2.4
B2	F	41	1.0	1.3	9	2.3
B3	F	41	0.0	0.0	0	0.0

It should be valuable at this point to compare the symptoms and behavior of these dogs during addiction and withdrawal with those found by Plant and Pierce. Symptoms during addiction will be considered first.

Weight. They found a rather rapid loss in weight for the first couple of weeks, while vomiting followed the injections. Three of our dogs gained weight during the first 15 days. The others lost weight, but began to regain it before they stopped vomiting. The weight changes during withdrawal are discussed elsewhere.

Vomiting. The dogs of Plant and Pierce vomited for a period of from five to 15 days at the beginning of the addiction. Our dogs did not vomit regularly after the first sixteen days. Plant and Pierce say: "As a rule when the vomiting had stopped, it did not return again until a very high dosage level was reached. We observed occasional vomiting at various times throughout the addiction period. This was probably reflex vomiting, and should be observed at least occasionally if it is a conditioned reflex. Contrary to the observations of Plant and Pierce our dog H1 did not vomit at all during the first four days of the addiction period. This is probably because the dose of morphine was quite small.

Salivation. Our experience with salivation was much the same as that of Plant and Pierce.

Narcosis. "All of our dogs showed marked diminution in the degree of narcosis produced by the daily administration of morphine, but none of them showed complete absence of narcotic effect, even where the administration was continued for more than 300 days."

"With an initial dose of 5 to 10 mgm. per kilogram the animal is deeply narcotized for three to six hours, during which it is difficult to arouse and if partially awakened, immediately sinks back into a relaxed comatose condition." Reference to Table II shows that none of our dogs were given as high as five mg. per kilogram of morphine sulphate at the start of the experiment. Also, Fig. 1 shows that the low initial dosages were continued for a period of eight days, until some tolerance had developed, before they were raised.

So, in complete contrast to the symptoms noted by Plant and Pierce our dogs were never narcotized, and the depressing effect after each injection did not manifest itself after a short time had elapsed. The condition observed by us simulates more closely the behavior of human addicts. The human addict often does not sleep well even at night.

Constipation. Both our dogs and those of Plant and Pierce showed varying degrees of constipation. Our dogs did not become so constipated as some of theirs did. We observed diarrhea on several occasions; Plant and Pierce do not mention this.

General Behavior. "All of our dogs were friendly and responsive to petting and easy to handle before the administration of morphine was begun. Three of them became somewhat cross and showed tendency to snap after tolerance was developed, but in none of these was the change sufficiently marked to make handling them difficult; the attendant was never bitten and in no case was a muzzle necessary. Two became quarrelsome with other dogs and had to be watched to prevent fighting in the runway. The majority were friendly, active, and responsive in the morning before the injection, but never as much so as before addiction was begun. Two became shy and seemed to avoid all contact with the attendant and with the other dogs but were not cross and could be handled without difficulty. The tolerant dogs seldom evidence any marked interest in other animals and although they occasionally played together in the runway, they more often held aloof. We never saw any evidence of heat in the females during addiction."

Our dogs were easy to handle at all times with the exception of C_1. C_1 was never cross or mean. With the exception of C_1 our dogs were friendly and responded to petting throughout the study. None of our dogs became quarrelsome with other dogs. Like two of the dogs mentioned above, C_2 became shy. B_3 was always interested in all of the other dogs except during the first week of withdrawal. C_1 showed an interest defect at all times.

Appetite. The appetites of our dogs were not so good as those of Plant and Pierce.

Hypersensitiveness and skin rashes. In avoiding most of the phenomena that Plant and Pierce report under this heading we more nearly approached the conditions observed in human beings. The skin of the human addict is very often decidedly hyposensitive. H_1 and C_1 developed slight hypersensitiveness.

Withdrawal symptoms will be compared now.

Tremors, twitching and rigidity in voluntary muscles. "The symptoms most frequently observed during withdrawal consisted in fine, fibrillary twitching in the muscles of the legs, back and head." These symptoms were not observed by us in H_1, B_1, B_2 and C_1, the dogs that were protected by sodium rhodanate. C_2 and B_3, not being protected by sodium rhodanate, exhibited both a gross head tremor and fibrillary twitching.

Groaning, howling and whining. Except for a little whining on the part of C_1 these symptoms were not seen in our dogs.

Restlessness. Many of the dogs that Plant and Pierce worked on exhibited restlessness of varying degrees of intensity. C_2 and B_3 were slightly restless and nervous at times. The restlessness was not accompanied by noisiness, but was rather intermingled with depression and disinterestedness. The dogs protected by sodium rhodanate did not appear restless or nervous.

Gnawing at objects within reach. This phenomenon probably can be classified as nervousness. C_1 exhibited it before and during the time that the dosage of morphine was being increased most rapidly. Several dogs showed slight tendencies to gnaw during withdrawal, especially B_3, which dog was not protected by sodium rhodanate.

Change in temperament and behavior. Our dogs did not become irritable and cross in contradistinction to some of those of Plant and Pierce. C_2 showed a distinct desire for the drug as did one of theirs. There were marked changes in the behavior of C_1; these will be considered separately.

Before abrupt withdrawal and while sodium rhodanate was being administered, B_1 and B_2 became somewhat disinterested and quiet. Since the withdrawal symptoms are due to the slow return of the nerves to normal after stopping morphine and a consequently protracted period of irritability, we can, if necessary, describe the behavior of B_1 and B_2 as due to withdrawal. Morphine was given in increasing dosage during this time. If the sodium rhodanate only partially overcame the effect of the morphine, partial peptization would occur with a consequent irritability of the nerves which can be manifested by depression and disinterest. In this manner the actions of B_1 and B_2 can be accounted for.

Hiccough. None of our dogs showed this symptom.

Photophobia. With the possible exception of C_1 during the time that he did not have enough sodium rhodanate, this symptom was not noticed.

Salivation. Plant and Pierce noted that salivation became less marked during withdrawal. We found the same thing in the cases of B_3, C_2, and C_1. On the other hand B_2, the protected dog, stopped salivating entirely for about eight days immediately after withdrawal. B_1, the other dog receiving sodium rhodanate salivated less than before withdrawal. After eight days these two dogs began to salivate more profusely than any of the others.

Vomiting. While Plant and Pierce observed vomiting in many of their dogs, only C_1 vomited during withdrawal; this was reflex in nature.

Muscular weakness, respiratory distress, panting, and sleepiness were not observed in any of our dogs.

Diarrhea. Plant and Pierce observed this in eight of their dogs. We observed it only in the two dogs that were not protected by sodium rhodanate.

Weight changes and pupillary reactions have already been described and discussed. Plant and Pierce observed only one dog that exhibited a desire for the drug. Schübel,[1] and Tatum, Seevers, and Collins,[2] have not observed a desire on the part of addicted dogs for the drug. The detailed study of this group of dogs presents many instances that can be interpreted as a desire for the drug. There seems to be no question but that the dogs liked the injections that they were given. A close study of the actions, reactions and habits of this group of dogs convinces us that most of them wanted, needed, and liked the drug after they became addicted.

The reactions of C_1 provide an exceptionally interesting behavior study. Not long before he came to us he was subjected to trauma, his right hind leg being injured. The effect of trauma is agglomeration. Before the start of the experiment he was observed to be a highly excitable, scatter-brained dog. He was hard to control, although not in any sense mean. When approached he tended to be suspicious. He showed no desire or care for human company or affection. He barked at the sky senselessly for long spells at a time. This is akin to the hypomanic state which consists of a condition of unstable irritability, poor discrimination, in which there is a quick reaction on the part of the stimulus response mechanism. The external and internal stimuli are reacted to more promptly than normal, but less thoroughly.

Eleven days on morphine quieted C_1 down. He was calm and less nervous; he was slightly more approachable, less wild, and ceased barking at the sky. He remained quiet for eight days. This stage is designated as "sedated hypomanic." In the manic depressive psychoses the sympathetic nervous system and its central correlations are agglomerated. Morphine acts first on the central nervous system. It can cause agglomeration in the central nervous system that will therefore mask the hypomania. Continued administration of morphine will finally agglomerate the affected sympathetic system intensifying the psychosis. In other words, the hypomania was masked

[1] Archiv exp. Path. Pharm., **88**, 1 (1920).

[2] J. Pharm. Exp. Ther., **36**, 460 (1929).

by the narcotic effect of the morphine, just as acute mania can be controlled, but not cured, by sodium amytal. The depressing effect of the morphine was noticeable during more than half of this period.

At the end of nineteen days a new condition became manifest. The dog was somewhat restless, and very unapproachable. He tended to stand faced away from human beings; sometimes with his head in the corner of his cage. There was an obvious hunted, maniacal look in the eyes of the dog during this period. It was difficult to give him injections during this time because he was so excitable. Upon soothing him the task was sometimes easier. This stage corresponds to the chronic mania stage of the manic depressive, manic psychosis, a more agglomerated condition than hypomania. The dog stayed in this stage for 20 days.

After withdrawing the morphine, sodium rhodanate was given for three days. This brought the dog back by peptization to a sedated hypomanic condition. The maniacal bearing disappeared and the dog quieted down. This is probably because the morphine was more rapidly eliminated from the sympathetic nervous system than from the central giving rise to a condition much the same as the original sedated hypomanic condition.

Sodium rhodanate was discontinued for one and one-half days. The maniacal bearing returned, and with it the state of chronic mania. Sodium rhodanate was administered for two days, and the dog returned to the sedated hypomanic condition. Two more days brought him into the original hypomanic state. Several months later the colloids of his nervous system returned to a normal degree of dispersion, having recovered from the trauma and the drug addiction. In this condition the dog persistently sought human affection, and cared for human company. He was easily approachable, and acted in every way like a normal dog.

On the other hand the dog may have been in a schizoid state, and overdispersed, trauma not being an etiological factor. Injections of morphine for eleven days, under this interpretation, returned the dog to normal due to the agglomerating action of morphine. Eight days more brought him into a condition resembling chronic mania, a condition which is due to agglomeration of certain of the protein colloids of the brain and sympathetic nervous system. Then, three days on sodium rhodanate peptized the colloids back to normal. The chronic mania reappeared when the sodium rhodanate was discontinued for a day and a half. Upon resumption of the administration of the peptizing agent the dog again returned to normal. He was then over-dispersed by the sodium rhodanate, going into the schizoid condition. Some months after the sodium rhodanate was stopped, the over-dispersed condition disappeared, and the dog returned to normal.

It does not seem necessary to insist that one or the other of these explanations is the correct one; the important thing is that there was a cycle of changes in behavior of the dog which paralleled the colloidal changes that were induced. The following diagram illustrates the cycle that this dog went through.

Hypomania   Sedated
or   —11 days→   Hypomania   —8 days→   Chronic
Schizoid   on Morphine   or   more   Mania
           Normal   on Morphine   20 days
           duration

↓ 3 days on NaCNS

Normal ← (Several Months No treatment) ... Sedated Hypomania or Normal ← 1 1/2 days without NaCNS

Sedated Hypomania or Normal

Hypomania ← 2 days more on NaCNS — Sedated Hypomania or Normal ← 2 days on NaCNS — Chronic Mania
or
Schizoid
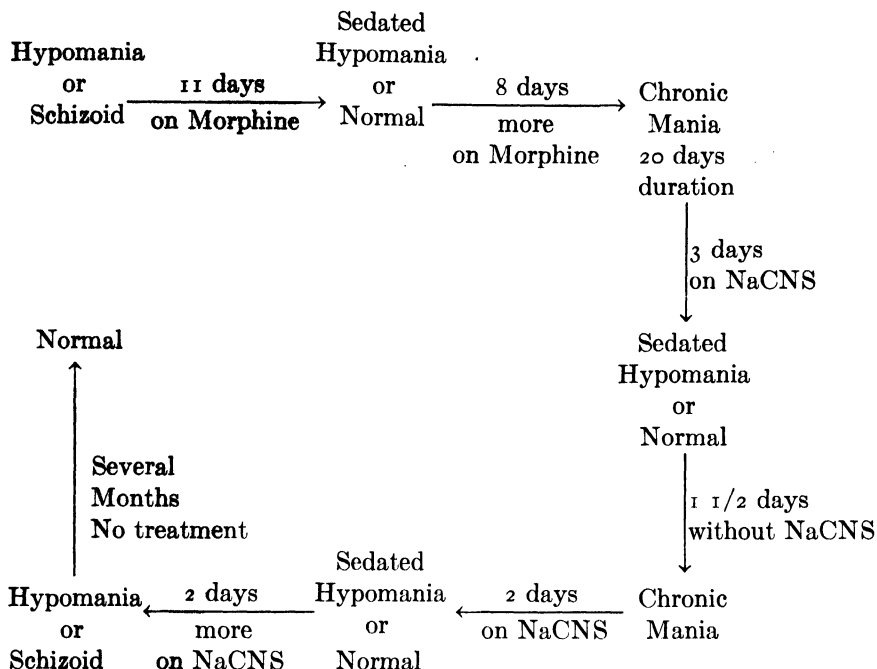
The object of this work has been realized because the dogs, C_2 and B_3, that were not given sodium rhodanate developed definite withdrawal symptoms. Whereas, C_1, B_1, and B_2 being protected by sodium rhodanate exhibited no withdrawal symptoms. It is regrettable that the effect of sodium rhodanate on the post-withdrawal craving can not be studied satisfactorily in animals for that is probably the most important part of the problem of drug addiction.

General Conclusions

1. Dogs can be addicted to small, increasing amounts of morphine; the picture produced is much the same as when larger amounts of the drug are used.

2. By using small doses of morphine the systemic upset produced is not so profound.

3. The behavior of the dogs during addiction and withdrawal indicates strongly that the demand of addicted tissue for morphine is reflected in a desire for the injected material.

4. As in human beings, some of the dogs were retarded by the drug. Likewise on dull, damp days the dogs were apparently depressed as many human addicts are.

5. Most of the phenomena observed by others during addiction were manifested by our dogs.

6. The theory requires that sodium rhodanate shall forestall or diminish greatly the withdrawal symptoms in addicted tissue because it should peptize rapidly the protein colloids that are agglomerated by morphine.

7. Sodium rhodanate was administered to addicted dogs one week prior to the abrupt withdrawal of morphine. During this time morphine was administered in ever-increasing doses.

8. These dogs were somewhat depressed at first. This may have been due to a disturbed condition brought about by the rapid peptization of the agglomerated colloids.

9. The dogs protected by sodium rhodanate exhibited no withdrawal symptoms upon the abrupt withdrawal of morphine. They gained a little weight.

10. The dogs not protected by sodium rhodanate were nervous, listless, lost weight, exhibited head and body tremors, had diarrhea and dilated pupils.

11. Sodium rhodanate does, in fact, prevent withdrawal symptoms in dogs addicted to small amounts of morphine, thus bearing out the theory.

12. One dog exhibited definite psychic changes as his protein colloids became more or less agglomerated; these changes were reversed. The dog went from one state of dispersion to another, and back again.

13. Withdrawal symptoms appeared in the dog just mentioned when sodium rhodanate was stopped. Resumption of the administration of the drug obliterated the symptoms.

14. Gnawing is not necessarily a withdrawal symptom.

15. It is to be expected from these experiments that the effects of morphine will be counteracted at least partially in the case of human beings by the use of sodium rhodanate.

Cornell University.

THE CATALYTIC ACTIVITY OF REDUCED COPPER CHROMATE AND OF VANADIUM OXIDE IN THE REDUCTION OF NITROCOMPOUNDS*

BY H. A. DOYAL[1] AND O. W. BROWN[2]

Introduction

The ability of finely divided platinum to promote certain oxidations was discovered by Davy and Doebereiner at the beginning of the nineteenth century. Near the latter part of the same century Sabatier and his co-workers began an extensive investigation of catalysis in the field of organic chemistry. Since that time numerous experiments have been carried out in many different laboratories, showing that a great number of diversified chemical reactions can be promoted by the use of suitable catalysts.

Since 1920, a series of investigations have been made in this laboratory, concerning the ability of finely divided metals and oxides to catalyze the reduction of nitrocompounds by hydrogen. This article gives the results of an investigation of the catalytic activity of reduced copper chromate and of vanadium oxide in the reduction of nitrobenzene to anilin. The activity was measured by the yields of amines and by the impurities which were present in the anilin.

Apparatus and Method of Procedure

The catalytic furnace used in this investigation was a horizontal type with an electrically heated bath consisting of lead-tin eutectic alloy, 75 atomic per cent of tin. The catalyst tube was an iron pipe, thirty inches in length and one inch in diameter. The design of the furnace and the method of operation are described in a previous publication[3] from this laboratory.

The ends of the catalyst tube were covered with a thick layer of asbestos to retard the leakage of heat and to prevent the condensation of the products in the delivery tube. The products were condensed in an air-cooled glass condenser. The excess hydrogen passed downward through a condenser drain tube and bubbled through 100 cc. of 1:1 HCl in a graduated liter flask. This was to prevent the escape of uncondensed anilin.

The catalyst was introduced into the furnace through an opening made by unscrewing the delivery tube. By means of a metal boat with a calibrated handle, a catalyst column ten inches long was placed inside the furnace. The outer end of this column was five and one-half inches inside the heating jacket of the furnace.

The temperature was measured by means of a copper constantan (advance) thermocouple which was inserted in a well surrounded by the metallic bath. This was calibrated against a standard thermocouple whose tip was placed inside the catalyst tube, five and one-half inches inside the heating jacket. During the calibration, air was passed through the furnace at the rate of 14 liters per hour.

Two cubic centimeter samples, measured by means of a calibrated pipette, were introduced into the furnace through a glass capillary. This capillary extended far enough into the catalyst tube to insure that the nitrobenzene was vaporized and would be carried over the catalyst by the hydrogen. The rate of flow of the nitrobenzene was regulated by means of a variable pressure which was obtained by changing the height of a mercury column, as described by Brown and Henke.[1] The rate of flow of hydrogen was measured by a calibrated flowmeter.

While the furnace was being heated to the desired temperature before an experiment and during the cooling which followed the completion of a series of runs, a current of hydrogen was continually passed through the furnace.

The hydrogen was allowed to flow for forty minutes, at the same rate as that used during the experiment, after the last of the nitrobenzene had entered the furnace. The amount of material still remaining in the furnace was very small and practically constant. Since the experiments were carried out without a time interval between them, this error was eliminated from all except the first run of a series.

After the furnace was "washed" with hydrogen 1:10 HCl was used to wash the products from the condenser into the graduated liter flask containing the 100 cc. of 1:1 HCl. This sample was then diluted to one liter and 100 cc. aliquot portions were titrated with tenth molar sodium nitrite solution. (This solution was standardized against pure catalytic ortho amido phenol.) Twenty cubic centimeters of conc. HCl were added before titrating. Starch iodide paper was used as an external indicator.

At room temperature the reaction is as follows:

$$C_6H_5NH_2 + HNO_2 \longrightarrow C_6H_5OH + N_2 + H_2O$$
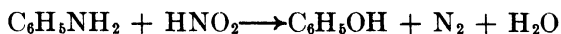
If the temperature is low the following reaction occurs:

$$C_6H_5NH_2 \cdot HCl + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$
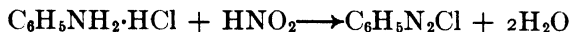
Since both reactions use the same amount of nitrous acid per mol of anilin the titration can be made at room temperature. Any other amines present would produce an error but this would be less than that introduced by purifying the anilin and weighing it.

All the yields given in this article are the average of from two to four consecutive experiments. The first run of each series is not included since it is generally either high or low, depending upon the previous history of the catalyst. The maximum variation of yields from these consecutive experiments is within one-half of one per cent.

[1] J. Phys. Chem., 26, 161, 272 (1922).

The quality of the anilin was investigated by collecting one run at each point of investigation. Part of this was let stand exposed to light for several days and the color changes noted. Part was placed on a watch glass in a drying oven at about 8o°C. After the anilin had evaporated the glass was examined for solid residue.

In order to purify the nitrobenzene, it was shaken with sodium carbonate solution, removed from the mixture by steam distillation, separated from the water in the distillate by decantation and dried with anhydrous calcium chloride. It was then distilled while in contact with fresh drying agent. The central constant boiling portion was redistilled. The middle portion of this distillate was used in this investigation.

The commercial hydrogen was purified by passing over red-hot copper, bubbling through concentrated sulphuric acid, passing through a caustic tower and then through a glass-wool filter.

PART I

Reduced Copper Chromate as a Catalyst

Preparation of the Catalyst

One hundred grams of Mallinckrodt's potassium dichromate were dissolved in about three liters of distilled water. Enough potassium hydroxide was added to convert the salt to potassium chromate. One hundred fifty grams of J. T. Baker's C. P. copper nitrate were dissolved in one and one-half liters of water. This solution was added to the potassium chromate solution while stirring rapidly. The precipitate was washed three times by decantation and then washed well on a Büchner funnel. It was then dried in an oven for about two days at 8o°C. The lumps were then ground into a coarse powder (through a ten mesh screen) and stored in a stoppered bottle until needed.

All copper chromate catalysts were prepared in the following manner unless otherwise specified. Fifteen grams of copper chromate were placed in the catalyst tube and reduced at 36o°C. for one hour with a rate of flow of hydrogen of 14 liters per hour.

Experimental Part

The data given in Table I show the effect of the rate of flow of nitrobenzene on the yield of amines.

Twenty runs were made before the above data were taken. Nitrobenzene was fed into the furnace at the rate of 3.55 grams per hour in these preliminary experiments. A new catalyst does not give constant yields during the first few runs.

Slow rates of flow of nitrobenzene produced a red-colored product. Tar-like substances condensed in the furnace exit-tube. The red color of the product and the tar gradually disappeared as the rate of flow of the nitrobenzene was increased.

TABLE I

Catalyst—reduced copper chromate.
Rate of flow of hydrogen—14 liters per hour.
Temperature—310°C.

Nitrobenzene Gms. per hr.	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.4	975	96.6
2.9	810	97.0
3.55	660	97.5
4.75	495	97.4
7.3	320	97.2
10.8	220	96.6

The best yields and the best products were obtained when 3.5 to 4.75 g. per hour of nitrobenzene were fed into the furnace. This anilin was clear with only a faint green color. Only a faint trace of solid residue remained when a small portion was evaporated on a watch glass. The sample which was titrated remained water white after titration. Many of the impurities gave colored products with sodium nitrite in the presence of hydrochloric acid. This showed that these substances were absent.

A deep green color replaced the green tint as the rate increased beyond 4.75 g. of nitrobenzene per hour. This color seemed to appear when the catalyst was being overloaded. This could be done either by feeding the nitrobenzene into the furnace too rapidly or by shortening the time of contact by increasing the rate of flow of the hydrogen. Anilin which had this deep green color reddened rapidly on standing in the light. The conditions under which the green appeared indicate that it was probably due to some intermediate reduction compound of nitrobenzene.

The figures given in Table II show the effect of the rate of flow of hydrogen on the yield of amines.

TABLE II

Catalyst—reduced copper chromate.
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—310°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
25	1180	96.7
20	940	97.7
14	660	98.3
10	470	98.8
5	235	98.7
3	140	98.3

Fifteen runs were made before the above data were taken.

The best yields and products were obtained when the rate of flow of hydrogen was ten liters per hour. When slower rates were used, the anilin had a reddish tint which darkened to a deep red on standing over night. When faster rates were used, the product had a deep green color. Here, again, this color appeared when the catalyst was overloaded.

The results given in Table III show the effect of temperature on the yield of amines.

<center>TABLE III</center>

<center>Catalyst—reduced copper chromate.</center>
<center>Rate of flow of nitrobenzene—3.55 g. per hour.</center>
<center>Rate of flow of hydrogen—10 liters per hour.</center>

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
381	86.4	297	98.4
349	94.3	282	98.1
333	96.9	246	96.0
310	98.8	237	80.9
		217	43.2

The product had a burnt orange color at high temperatures. This color gradually disappeared as the temperature was lowered. After four runs at 310°C., the product was clear and the only color was a faint tinge of green. Below 310°C., the green gradually darkened.

Below 310°C., the yield of anilin decreased as the temperature became less. Two things indicate that this was due to a decrease in the activity of the catalyst. The first was the appearance of the green color. The second was the appearance of nitrobenzene in the products. One method of detecting its presence was by its odour. Another was by the characteristic taste of nitrobenzene that one obtained from the vapors while pipetting aliquot samples for titration. Below 246°C., a black tarry amorphous precipitate appeared in the hydrochloric acid solution. It also appeared in the delivery tube of the furnace. Nitrobenzene, highly colored with impurities, collected at the bottom of the solution of anilin-hydrochloride.

Above 310°C., the yield of anilin also decreased. Apparently, since no nitrobenzene was found in the products, this decrease in yield was not due to too little activity but rather to too much activity on the part of the catalyst. Above 400°C., the volume of the condensed liquid products decreased rapidly. When operating at these high temperatures, a white smoke poured out of the delivery tube of the furnace. This smoke condensed neither in the air-cooled glass condenser nor in the 1:1 HCl in the graduated liter flask but was carried out into the air by the excess hydrogen.

Traces of products, probably due to consecutive reactions, increased with the temperature (above 310°C.). At 381°C. enough diphenylamine was produced to give a slight precipitate when the anilin-hydrochloride solution was diluted to one liter. At temperatures below 381°C., there was enough

of the secondary amine present to give the solution a purple color after titration with sodium nitrite. After two or three runs were made at 297 to 282°C., no test for diphenylamine could be obtained. After running at temperatures in the neighborhood of 400°C., several runs were necessary before the product failed to give a test for this secondary amine when the temperature of the furnace was maintained at 310°C.

The curves in Fig. 1 show the relation between the temperature and the yield of amines with a reduced copper chromate, a copper and a chromium
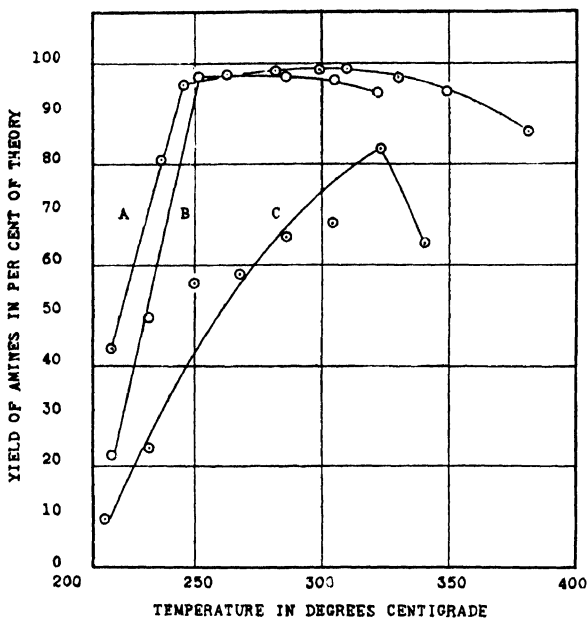
FIG. 1

catalyst. The data for the copper and chromium were obtained from previous publications[1] from this laboratory.

Curve A shows the yields obtained over a reduced copper chromate catalyst. The yields for a copper catalyst are plotted in curve B and for chromium in curve C.

It is seen, from the curves, that the action of the reduced copper chromate catalyst more closely resembles that of copper than of chromium. The products also indicated this.

Three catalysts were prepared from copper chromate. Fifteen grams were used in each case. The first was heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The second was heated in a current of hydrogen, 14 liters per hour, at 460°C. for one hour. The third was first heated in a current of air at 460°C. for two hours and then heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The three catalysts

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[1] J. Phys. Chem., **26**, 161, 272 (1922).

were run at 310°C. until constant yields were obtained. The rate of flow of nitrobenzene was 3.55 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The first catalyst produced 98.7 per cent of anilin. The second gave yields which averaged 96.5 per cent and the third produced 99 per cent of anilin. This shows that the yield of anilin can be decreased by heating the catalyst in hydrogen at 460°C. The anilin produced by such a catalyst is opaque. Previous heating in air at 460°C. seemed to have little effect on the yield and quality of the anilin. The products obtained by the use of the first and third catalysts were clear and almost white. The only color was a faint trace of green. There was only a slight trace of solid residue remaining after the anilin was removed by evaporation at about 80°C. The solution of anilin-hydrochloride remained water white after titration with sodium nitrite. The anilin, without purification by distillation, when protected from the light would remain without any appreciable color change for three or four days. At the end of three weeks, it was still clear but had acquired a light red color.

Anilin produced under unfavorable conditions was opaque and not clear. This was due to finely divided impurities in suspension. The addition of two drops of nitrobenzene to 2 cc. of anilin will produce a red color in a few minutes. This explains why the anilin which contained traces of nitrobenzene was red. Other impurities were produced at high temperatures which also gave the product a red color.

PART II

The Catalytic Activity of Vanadium Oxide in the Reduction of Nitrocompounds

A few experiments, using a lower oxide of vanadium as a catalyst, were carried out[1] in this laboratory in 1922. The maximum yield of anilin obtained by the reduction of nitrobenzene was 88 per cent of theory. The following experiments were carried out to investigate the activity of this catalyst.

The catalysts were prepared by the ignition of ammonium meta-vanadate, C. P., purchased from the S. W. Shattuck Chemical Co., Denver, Colorado.

The effect of the rate of flow of hydrogen on the yield of amines is shown by the results given in Table IV.

TABLE IV

Catalyst—15 g. V_2O_5 reduced in hydrogen (é).
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—403°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
20	940	80.8
14	660	83.9
10	470	79.5

[1] J. Phys. Chem., **26**, 283 (1922).

(é) *Preparation of the catalyst.* Ammonium meta-vanadate was placed in a porcelain dish and ignited in an electric muffle at 275°C. for three hours. During the heating the catalyst was stirred frequently. The muffle was provided with two openings for the circulation of air. The resulting black powder was placed in a cold catalytic furnace. The temperature was gradually raised to 460°C. where it was maintained for two and one-half hours. During this time, hydrogen was passed through the furnace at the rate of 14 liters per hour. The catalyst was probably a lower oxide of vanadium.

Fifteen runs were made with this catalyst at 403°C. before the data for Table IV were taken. Constant results were not obtained during the first runs. The product from these first runs was green and no precipitate could be detected in the anilin-hydrochloride solution. The color became lighter after the first few runs and a precipitate containing diphenylamine appeared in the 1:1 HCl in the liter flask. No precipitate appeared in the glass condenser since this secondary amine is somewhat soluble in anilin.

The diphenylamine was identified by the following properties:

1. It was almost insoluble in dilute acids and its solubility increased with the concentration of the acid. It was soluble in concentrated hydrochloric or concentrated sulphuric acid.

2. When sodium nitrite or some other oxidizing agent was added to its solution in concentrated sulphuric acid an intense blue color appeared. At lower concentrations, varying shades of color from blue to light purple appeared.

3. The crystals were flat plates. The melting point was not sharp but was from 55° to 65°C. This was due to impurities and to decomposition products caused by the exposure of the amine to the air and to traces of HCl which was used to remove the anilin.

4. When the crystals were moistened with dilute hydrochloric acid they turned blue on exposure to the air for a few hours.

The presence of this secondary amine introduced an error in the determination of amines, since one mol of diphenylamine combines with the same amount of nitrous acid as one mol of anilin. When the solution of anilin in 1:1 HCl was diluted to one liter, part of the dissolved diphenylamine precipitated. Most of the precipitate was in a state of fine division and remained in suspension. Since part of the secondary amine was still in solution no attempt was made to remove the rest by filtration. Even under the most favorable conditions for the production of diphenylamine less than five per cent of it was produced. When the conditions were favorable for the production of anilin this error was less than one-tenth of one per cent. The presence of the precipitate made the end point of the titration rather slow since more of the precipitate dissolved as that in solution was removed by the titration. In acid solution, the following reaction takes place during titration.[1]

$$(C_6H_5)_2NH + HNO_2 \longrightarrow (C_6H_5)_2N \cdot NO + H_2O$$

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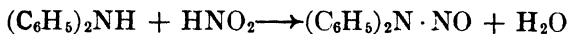
[1] Bernthsen and Sudborough: "Text-book of Organic Chemistry," 404 (1930).

The best yield of amines was obtained with this catalyst when hydrogen was passed into the furnace at the rate of 14 liters per hour. When a rate of ten liters per hour was used the precipitate of diphenylamine increased. When samples of the anilin were taken most of this secondary amine was dissolved in the solvent, but part of it remained in suspension. This caused the solution to be opaque. The sample darkened rapidly. This was more noticeable when it was exposed to a strong light.

The production of diphenylamine seems to be a consecutive reaction and not a side reaction. If a catalyst promotes consecutive reactions, then increasing the time of contact with the catalyst should increase the amount of the substances which are formed by the consecutive reactions. This fact and the results shown in Table IV and Table V lead the authors to believe that the production of the diphenylamine is a consecutive reaction. It probably takes place in the following manner.

$$2 \ C_6H_5NH_2 \longrightarrow (C_6H_5)_2NH + NH_3$$
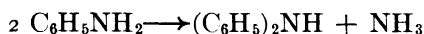
Diphenylamine was produced in all of the experiments listed in Table IV. When the rate of flow of hydrogen was increased to twenty liters per hour the yield of both anilin and diphenylamine decreased.

The effect of nitrogen on the activity of vanadium oxide is shown in the results given in Table V.

TABLE V

Catalyst—15 g. of reduced V_2O_5, prepared in the same manner as described following Table IV

Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of gas—14 liters per hour.
Temperature—403 °C.

Nitrogen Liters per hour	Hydrogen Liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
0	14	660	83.8
4	10	470	80.8
10	4	190	73.7

In this case, the rate of flow of the gases was kept constant and the partial pressure of the hydrogen was varied. The effect which the nitrogen had on the adsorption of the hydrogen and the nitrobenzene is not known. This should be specific and should depend on the nature of the catalyst used and on the other substances present. The yield of amines was decreased by the presence of the nitrogen. If the variation in the amount of hydrogen made any change in the amount of diphenylamine produced, this difference was too small to be detected by inspection of the precipitate.

The data given in Table VI show the effect of temperature on the activity of a vanadium oxide catalyst.

TABLE VI

Catalyst—15 g. of reduced V_2O_5, prepared as previously described.

Rate of flow of hydrogen—14 liters per hour.

Rate of flow of nitrobenzene—3.55 g. per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yields of amines in percent of theory. Calculated as anilin
489	35.1	403	81.3
442	61.0	393	75.0
425	66.9	368	54.7
413	75.1	336	30.2

Fifteen runs were made with this catalyst at 403°C. before the data for Table VI were taken. All anilin produced above 393°C. contained diphenylamine. The amount increased as the temperature increased. No clear aniline was produced with a vanadium oxide catalyst prepared in this manner. The opacity of the aniline was due to impurities which were in suspension.

The anilin was black when the temperature was allowed to drop a few degrees below 403°C. A tarry product condensed in the delivery tube of the furnace. It was this substance which produced the color in the anilin. Tests showed that this tar was only slightly soluble in alcohol, ether or gasoline, but was fairly soluble in anilin. When several runs were made at lower temperatures the formation of this tar decreased rapidly but never ceased entirely. This was very similar to the action of reduced copper chromate at temperatures below 246°C. As the amount of tar produced decreased the black color of the product gradually changed to red. The red color was probably due to traces of nitrobenzene in the product. The amount of nitrobenzene increased as the temperature decreased. When the catalyst was used at temperatures as low as 336°C. large drops of nitrobenzene collected at the bottom of the anilin-hydrochloride solution. The catalytic activity of this catalyst, at temperatures below 403°C. seems to decrease as the temperature decreases. The red color of the anilin produced at low temperatures is similar to the color produced when nitrobenzene is added to anilin.

Although nitrobenzene was found in the products at lower temperatures, none was detected in the mixture at higher temperatures. Products from consecutive reactions, such as diphenylamine appeared at higher temperatures but they did not appear when the catalyst was used at lower temperatures.

Experiments were conducted to determine the effect of heating the V_2O_5 in air at 400°C. before it was reduced in hydrogen. After the V_2O_5 was heated in a current of air at 400°C. for one hour, 15 g. of the material were placed in the catalyst tube and reduced by heating in hydrogen for two and one-half hours at 460°C. The rate of flow of hydrogen was 14 liters per hour. Fifteen runs were made before the data were taken. The yields from this catalyst are shown in Table VII.

TABLE VII

Catalyst—15 g. of reduced V_2O_5.

Rate of flow of nitrobenzene—3.55 g. per hour.

Rate of flow of hydrogen—14 liters per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
415	80.8	398	86.8
408	87.7	378	77.2
403	89.3	360	67.9

The results in Table VII show that heating to 400°C. in air increased the production of anilin. Less diphenylamine was produced by this catalyst than by the ones prepared by heating in air to only 275°C. The anilin produced by the use of this catalyst was opaque due to impurities in suspension.

A catalyst was prepared by heating ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the V_2O_5 produced were placed in a catalytic furnace and heated in a current of hydrogen, fourteen liters per hour, at 460°C. for two and one-half hours.

A study of the effect of the rate of flow of nitrobenzene on the yield of amines was made with this catalyst. Table VIII shows the results obtained. Fifteen runs were made before the data for this table were taken.

TABLE VIII

Catalyst—reduced V_2O_5.

Temperature—403°C.

Rate of flow of hydrogen—14 liters per hour.

Nitrobenzene Gms. per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.37	970	90.9
2.85	805	91.3
3.55	660	91.7
4.90	480	91.8
7.10	330	88.3

The color of the anilin was a cherry red when slow rates of feed of nitrobenzene were used. The purple color due to the reaction of diphenylamine and sodium nitrite, appeared in the solution of anilin-hydrochloride after the titration had been made. Tarry substances condensed in the delivery tube of the furnace.

As faster rates were used, the product gradually lost its red color. When 7.1 g. per hour of nitrobenzene were fed into the furnace the product was a yellowish green. The color as well as the decrease in the yield of amines indicates that the catalyst was overloaded.

The anilin produced when 3.5 to 4.9 g. per hour of nitrobenzene were fed into the furnace was almost clear. A test for diphenylamine could be obtained by evaporating the anilin at about 80°C. and dissolving the solid residue in a few drops of concentrated sulphuric acid. The addition of a drop of sodium nitrite solution produced a deep blue color.

Discussion of Results

When the flow of nitrobenzene was kept constant, the furnace maintained at the most favorable temperature and the rate of flow of hydrogen was varied, an intermediate rate was found to give the highest yield of amines in per cent of theory. A high velocity of the hydrogen seemed to cause incomplete reduction. In the horizontal furnace, the contact between the reacting gases and the catalyst is brought about by the diffusion of the gases and convection currents. The heat of reaction and, possibly, the heat of adsorption cause the temperature of the catalyst to become higher than that of the rest of the furnace. The heat of reaction in the reduction of nitrobenzene to anilin is 98.8 Calories per mol. The vapors in contact with the wall of the furnace also become hotter than the rest. This difference in temperature causes the convection currents. The concentration of the nitrobenzene vapor in the original gaseous mixture is decreased next to the catalyst since it, in addition to part of the hydrogen, is continually being removed by the chemical reaction. This would cause diffusion of the nitrobenzene toward the catalyst. Probably, a high velocity would carry some of the nitrobenzene vapor through the furnace without its being in contact with the catalyst.

When the velocity of the vapors was too low there was too long a contact with the catalyst, which reduced the yield of anilin. The red color and the opacity of the products, neither of which was due to nitrobenzene or anilin, indicate that the decrease in yield was due to the formation of other compounds. When a vanadium oxide catalyst was used one of these compounds was shown to be diphenylamine.

In addition to velocity, the ratio of nitrobenzene to hydrogen is a factor which must be considered in the production of anilin. When the rate of flow of hydrogen was kept constant and the amount of nitrobenzene was varied an intermediate rate of flow of nitrobenzene was found to be the most favorable for the production of anilin. (See Tables I and VII). When low rates of flow of nitrobenzene were used, the product was red and opaque. A tar-like substance with a high boiling point condensed in the delivery tube of the furnace. When sufficiently high rates were used nitrobenzene could be detected in the products. Thus, low rates favor the formation of impurities in the anilin while high rates cause incomplete reduction of the nitrobenzene. The most favorable rate of flow of nitrobenzene and of hydrogen depends upon the amount and the nature of the catalyst used.

The effect of the temperature has been described following Tables III and VI.

When these catalysts, which had been working under favorable conditions for the production of anilin, were used at sufficiently low temperatures a large quantity of tarry substances appeared in the products. However, the amount of tar decreased with each successive run until only a trace remained. In the case of reduced copper chromate, the temperature drop required was about 70°C. below the most favorable temperature for the production of anilin. When vanadium oxide was used a drop of about 15°C. was sufficient to promote the formation of these tars.

Conclusion

I. The highest yield of amines obtained with a reduced copper chromate catalyst was 99 per cent of theory. This yield was obtained at 310°C. with a flow of hydrogen of 14 liters per hour and a rate of flow of nitrobenzene of 3.55 g. per hour. The catalyst used was prepared by heating copper chromate in air at 460°C. and then reducing it in a current of hydrogen, 14 liters per hour, at 360°C.

II. The highest yield of amines obtained with a reduced vanadium oxide catalyst was 91.8 per cent of theory. This yield was obtained at 403°C. with the rate of flow of nitrobenzene 4.9 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The catalyst was prepared by igniting ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the vanadium pentoxide produced were placed in a cold catalytic furnace and heated in a current of hydrogen, 14 liters per hour, at 460°C. for two and one-half hours.

III. Diphenylamine was shown to be one of the products which was produced by both catalysts. Vanadium oxide was shown to be a better catalyst than reduced copper chromate for the production of diphenylamine.

IV. The substitution of nitrogen for part of the excess hydrogen was shown to decrease the yield of amines when a vanadium oxide catalyst was used.

V. Reduced copper chromate was shown to be a better catalyst for the production of anilin than vanadium oxide. The ability of reduced copper chromate to promote the production of a high grade anilin was shown.

VI. The relative amounts of nitrobenzene and hydrogen, the velocity of the gases as they passed over the catalyst and their temperature were shown to be important factors in the production of secondary products.

Laboratory of Physical Chemistry,
Indiana University, Bloomington.

ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

I. The Decomposition of Mixtures of Dimethyl and Diethyl Ether

BY E. W. R. STEACIE

Introduction

In a homogeneous unimolecular gas reaction, the reacting molecule undoubtedly acquires the energy of activation by a redistribution of energy between molecules at collisions. It is a fundamental characteristic of such reactions that the velocity constants decrease at low pressures. At such pressures the time required for an activated molecule to react becomes comparable with the time between collisions. At low partial pressures of the reactant, collisions with inert gases would naturally be expected to be effective in maintaining the rate of reaction. It is an experimental fact, however, that the effect of inert gases is highly specific. Hydrogen and the reaction products are usually highly effective in maintaining the rate, while other foreign gases are usually quite ineffective.

The highly specific nature of the effect is somewhat puzzling, although the question has received considerable attention from the point of view of quantum mechanics.[1] If statistical redistribution of energy occurred during a single collision between a molecule of inert gas and an activated molecule of reactant, then, since almost all activated molecules have energy only slightly in excess of the energy of activation, deactivation should result in virtually every collision. This should be the case even with comparatively simple inert gases with a small number of degrees of freedom.[2] Since this is not the case with the majority of inert gases, it is necessary to assume a high specificity of energy transfer during collisions of the second kind.

It would naturally be expected that complex molecules with a number of internal degrees of freedom comparable to that of the reactant would be more effective in maintaining the rate than would simple gases. It would also be expected that statistical redistribution would be more easily established between molecules which resemble one another in structure and in chemical properties, since such redistribution is apparently easily established between molecules of the reactant itself. Up to the present, however, all investigations of the effect of foreign gases on unimolecular reactions have been confined to comparatively simple gases.

The decompositions of the various aliphatic ethers which have been investigated by Hinshelwood and his co-workers,[3] offer ideal material for the

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[1] Kallmann and London: Z. physik. Chem., **B2**, 207 (1929); Zener: Phys. Rev., (2) **37**, 556 (1931); O. K. Rice: Chem. Reviews, **10**, 125 (1932).

[2] O. K. Rice: Réunion internationale de chimie physique, Paris, Oct. **1928**, p. 305; Kassel: "Kinetics of Homogeneous Gas Reactions," 111 (1932).

[3] Hinshelwood: Proc. Roy. Soc., **114A**, 84 (1927); Hinshelwood and Askey: **115A**, 215 (1927); Hinshelwood and Glass: J. Chem. Soc., **1929**, 1804.

investigation of the mutual influence of similar complex molecules. An investigation has therefore been commenced on the thermal decomposition of mixtures of various ethers, as announced in a preliminary communication.[1] The present paper deals with the first pair which has been investigated, viz. dimethyl and diethyl ether.

Experimental Procedure

The reaction velocities were followed in the usual way by admitting the reactant, or reactants, to a heated silica bulb connected to a capillary manometer and noting the change in pressure with time. The apparatus was identical with one which has been previously described.[2]

Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge "Workshop Pattern" potentiometer. The temperature was controlled by the hand regulation of rheostats, and could be maintained constant to within 0.5°C.

Methyl ether was prepared from sulphuric acid and methyl alcohol in the usual way. The gas was freed from unchanged methyl alcohol by bubbling through sulphuric acid saturated with methyl ether. It was then dried by passage through tubes containing phosphorus pentoxide, and fractionally distilled. During the course of the experiments it was stored as a liquid in a bulb immersed in a carbon dioxide-acetone mixture.

Ethyl ether was purified by shaking with sulphuric acid. It was then dried over sodium and fractionally distilled (B. P. 34.5°C). It was stored in a bulb over sodium. To prevent contamination by tap grease this bulb was also immersed in a carbon dioxide-acetone mixture.

Experimental Results

Since the falling off in rate at low pressures is only very slightly influenced by temperature, it was not considered worth while carrying out experiments over a range of temperatures. Accordingly all experiments were made at 478°C, at which temperature both ethers decompose at convenient rates.

According to the mechanisms postulated by Hinshelwood, the reactions are mainly as represented by

$$CH_3OCH_3 = CH_4 + CO + H_2,$$

and

$$C_2H_5OC_2H_5 = C_2H_6 + CO + CH_4.$$
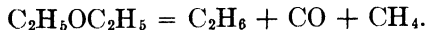
Hydrogen is the only reaction product which has any effect in maintaining the rate. This introduces a certain complication when dealing with mixtures, inasmuch as the hydrogen formed in the decomposition of methyl ether will influence the rate of decomposition of ethyl ether. In order to minimize this effect all measurements were made in the early stages of the reaction, the rates of reaction being inferred from a comparison of the times for a 25 percent increase in pressure of the reactant or reactants.

[1] Steacie: J. Am. Chem. Soc., **54**, 1695 (1932).
[2] Steacie: Can. J. Research, **6**, 265 (1932).

The Effect of Surface.

In agreement with the results of Hinshelwood, it was found that the decomposition of both ethers is predominantly homogeneous. Experiments in a bulb packed with short lengths of silica tubing showed that the surface reaction was negligible.

The results which follow were obtained in random order. A few runs were made with methyl ether alone, then with ethyl ether, the mixture, and so on. In each series the runs were also made in random order as regards pressure.

(a). Pure Ethyl Ether.

The values of T_{25} for pure ethyl ether at 478°C are given in Table I.

<div align="center">

TABLE I

Pure Ethyl Ether

</div>

Pressure, cms.	6.30	6.82	8.54	8.75	10.01	11.16	11.80
T_{25}, mins.	29.5	29.5	27.0	26.8	24.2	24.5	24.4

Pressure, cms.	14.39	16.15	16.60	16.88	17.83	17.98
T_{25}, mins.	23.1	21.4	22.5	21.9	21.5	20.5

Pressure, cms.	20.29	22.18	25.80	28.02	28.30	31.05	31.20
T_{25}, mins.	20.6	20.1	17.6	16.3	17.0	16.7	15.8

Pressure, cms.	32.07	32.75	37.06	37.55	38.40	53.80
T_{25}, mins.	16.8	16.0	15.0	14.8	15.6	13.3

The results given in Table I are plotted in Fig. 1. In order to obtain a convenient curve for interpolation, it is desirable not to have too great curvature. Fig. 1, therefore, gives T_{25} plotted against $1/p$, rather than against p.

The falling off in rate shown in Table I and Fig. 1 is in practically exact agreement with that previously found by Hinshelwood. The absolute value of the velocity is slightly greater than that of Hinshelwood. We may calculate the rate at infinite pressure to a fair approximation by a linear extrapolation of Fig. 1. Treating Hinshelwood's data in a similar way for 504°C, and using his value for the heat of activation, we obtain about 11.4 mins. for T_{25} at 478°C. The value from Fig. I is about 9.0 mins. The difference may in part be due to the uncertainty in extrapolating to infinite pressure. In any case it corresponds to a discrepancy of only about 2° in temperature between the two investigations.

(b). Pure Methyl Ether.

The results for pure methyl ether at 478°C are given in Table II.
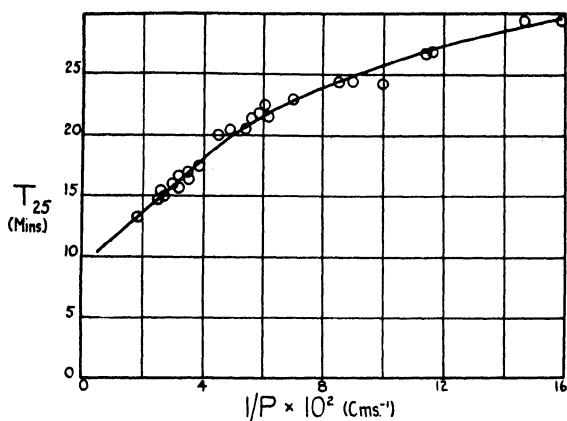
FIG. 1

Ethyl Ether

TABLE II

Pure Methyl Ether

Pressure, cms.	6.31	8.45	10.37	12.03	13.32	17.85	18.25	18.70
T_{25}, mins.	45.6	36.3	33.7	30.0	27.5	25.0	25.0	23.5

Pressure, cms.	28.30	30.90	38.10	39.34	46.40	50.30	59.40
T_{25}, mins.	21.4	20.6	19.9	19.5	19.1	17.8	16.8

Pressure, cms.	63.35	65.30
$T_{,25}$ mins.	16.8	16.7
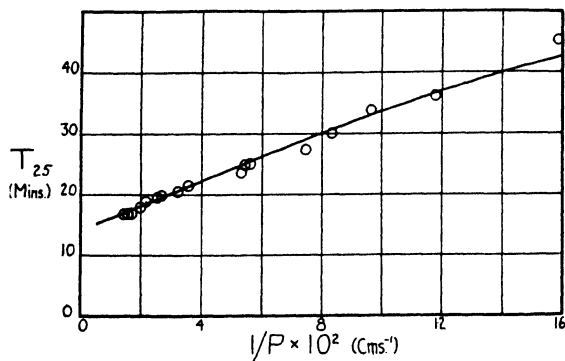
FIG. 2

Methyl Ether

The data of Table II are plotted in Fig. 2 in the same way as those for ethyl ether. As with ethyl ether, the falling off in rate with decreasing pressure is similar to that found by Hinshelwood. A comparison of the calculated high pressure rates at $478°C$ gives 13.5 mins. from Fig. 2, as against about 14.2 minutes from Hinshelwood's data. The discrepancy is within the experimental error, since it corresponds to a temperature difference of about $0.5°C$.

FIG. 3
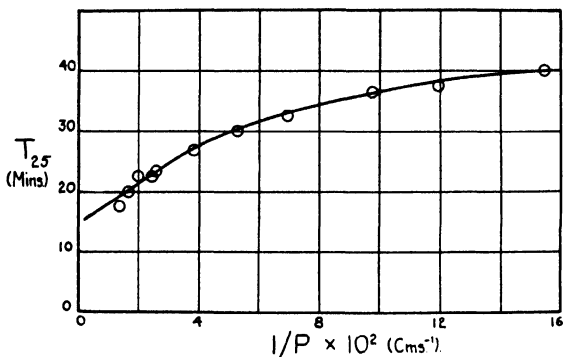
1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3
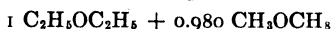
(c).   *Mixtures of Methyl and Ethyl Ether.*

Having established the rates for the separate ethers over the range of pressure, a series of runs were made with a mixture consisting of 1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3. The times for the total pressure of the mixture to increase by 25 percent are given in Table III.

TABLE III

1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3
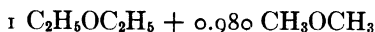
Total pressure, cms.	6.44	8.33	10.20	14.95	18.95	26.05
T_{25}, mins.	39.7	37.5	36.6	32.5	30.0	26.8

Total pressure, cms.	38.26	40.05	50.58	58.83	71.10
T_{25}, mins.	23.2	22.6	22.7	20.0	17.3

The results are plotted as before in Fig. 3.

In Table IV the observed results for the mixture are compared with those calculated from the rates of decomposition of the separate reactants on the assumption (a) that the two substances have zero efficiency in so far as mutual activation is concerned, and (b) on the assumption that the efficiency is 100 percent. The manner in which the values in Table IV are arrived at may be illustrated by a sample calculation, using the figures given in the first line of the table.

TABLE IV

Description								
Total pressure, cms.	71.10	58.83	50.58	40.05	38.26	26.05	18.95	14.95
T_{25}, mins.	17.3	20.0	22.7	22.6	23.2	26.8	30.0	32.5
T_{25} for pure methyl ether at a pressure equal to the partial pressure in the mixture.	20.2	21.2	22.5	24.3	25.0	29.5	35.5	40.8
T_{25} for pure ethyl ether at a pressure equal to the partial pressure in the mixture.	15.5	17.0	18.1	20.1	20.4	23.3	27.7	28.3
Percent increase in total pressure in the time given in column 2, due to methyl ether.	10.5	11.5	12.3	11.4	11.4	11.2	10.5	9.8
Percent increase in total pressure in the time given in column 2, due to ethyl ether.	14.3	15.0	16.0	14.0	14.5	14.6	14.0	14.7
Calculated fractional change in the time given in column 2.	24.8	26.5	28.3	25.7	25.9	25.8	24.5	24.5
Ratio $\dfrac{\text{calculated change,}}{\text{observed change}}$ assuming zero efficiency.	0.99	1.06	1.13	1.02	1.03	1.03	0.98	0.98 — mean = 1.03
T_{25} for pure methyl ether at a pressure equal to the total pressure of the mixture.	16.8	17.4	18.0	19.2	19.5	22.0	24.6	27.5
T_{25} for pure ethyl ether at a pressure equal to the total pressure of the mixture.	11.2	12.5	13.4	14.8	15.0	18.1	20.5	22.5
Percent increase in total pressure in the time given in column 2, due to methyl ether.	12.7	14.1	15.6	14.5	14.6	15.0	15.0	14.5
Percent increase in total pressure in the time given in column 2, due to ethyl ether.	19.5	19.1	21.3	19.4	19.6	18.8	18.6	18.3
Calculated fractional change in the time given in column 2.	32.2	33.2	36.9	33.9	34.2	33.8	33.6	32.8
Ratio $\dfrac{\text{calculated change,}}{\text{observed change}}$ assuming 100 per cent efficiency.	1.29	1.33	1.48	1.36	1.37	1.35	1.34	1.31 — mean = 1.36

It is found experimentally that when the total pressure of the mixture is 71.10 cms. the value of T_{25} is 17.3 minutes. The partial pressure of methyl ether in the mixture is 35.21 cms., that of ethyl ether is 35.89 cms. From Figs. 1 and 2, the values of T_{25} for the pure substances at these pressures are 20.2 and 15.5 mins., respectively. If we assume zero efficiency in mutual activation, the substances will decompose at rates corresponding to these values when mixed. In the time required for a 25 percent increase in pressure of the mixture, viz. 17.3 mins., the methyl ether present will therefore decompose to an extent corresponding to a time equal to 17.3/20.2 of T_{25}. From a typical rate curve for methyl ether, this corresponds to 21.3 percent increase in pressure. Similarly, in 17.3 mins. the percent pressure increase for ethyl ether will be 28.0. Hence, taking into consideration the relative quantities of the two substances, we find that the increase in total pressure due to the decomposition of methyl ether will be 10.5 percent in 17.3 minutes, while that due to ethyl ether will be 14.3 percent. Hence, the calculated pressure increase in 17.3 mins. is 24.8 percent, as against an observed increase of 25 percent.

The calculations for 100 percent efficiency are carried out in the same way, except that it is assumed that each reactant will decompose at a rate corresponding to a pressure of the pure substance equal to the total pressure of the mixture.

It will be seen that the average value of the ratio

$$\frac{\text{percent change calculated}}{\text{percent change observed}},$$

assuming zero efficiency in mutual activation, is 1.03. Considering the number of different experimental values involved in the calculation, this certainly constitutes an agreement within the experimental error. The difference of 0.03 found is actually in the wrong direction, i.e. the mixture decomposes more slowly than the calculated rate.

On the assumption of 100 percent efficiency, the average value of the above ratio is 1.36. In other words, if 100 percent efficiency in activation occurred the mixture should decompose at a rate nearly 40 percent faster than the observed value.

It may therefore be concluded that if either of the reactants has any effect in keeping up the rate of the other, the effect is smaller than the experimental error of the present investigation, and is probably not more than 5 percent of the effect due to collisions between molecules of the same kind.

Discussion

The work of Zener, Kallmann and London, and Rice, previously referred to, has given indications of a theoretical basis for the high specificity of energy transfer during collisions of the second kind. This gives at least a partial explanation of the high efficiency of hydrogen compared with nitrogen, helium, etc. It offers no explanation, however, for the high specificity when dealing with molecules of a foreign gas whose complexity is of the same order of magnitude as that of the reactant.

There is, however, some indication of a similar specific energy transfer between complex gas molecules and a solid surface. Thus there appears to be a high efficiency of energy transfer in producing activated molecules by collisions of acetone and diethyl ether with platinum.[1] On the other hand, collisions of propionaldehyde and of dimethyl ether with platinum are comparatively inefficient in establishing statistical distribution of energy.[2] In such cases, however, we are dealing with collisions between two substances of a quite different nature.

The low efficiency of energy transfer in the case of the two ethers is, however, very surprising. The chemical and physical properties of the two substances are very similar. Their modes of decomposition are almost identical, in each case involving the splitting off of a hydrocarbon, followed by the loss of carbon monoxide by the resulting aldehyde, viz.

$$CH_3OCH_3 = CH_4 + HCHO = CH_4 + CO + H_2,$$
and
$$C_2H_5OC_2H_5 = C_2H_6 + CH_3CHO = C_2H_6 + CO + CH_4.$$

The activation energies of the two processes are also of the same order of magnitude, being 58,500 and 53,000 calories, respectively. The falling off in rate with pressure is slightly different for the two substances, and leads to the conclusion that 15 squared terms are required to account for the decomposition of dimethyl ether, and 8 for diethyl ether. If the number of squared terms were a measure of the efficiency of energy transfer, we might not expect ethyl ether to be effective in maintaining the rate of decomposition of methyl ether, but it would certainly be expected that methyl ether would be effective in preventing the falling off in rate of ethyl ether.

We are therefore led to the conclusion that the efficiency of energy transfer must be governed by the actual groups participating in the collision, rather than by the general nature of the molecule as a whole. Presumably collisions between methyl groups or ethyl groups are effective, but not collisions between a methyl group and an ethyl group. From this point of view, considerable information might be gained from the investigation of mixtures of methyl ethyl ether with dimethyl ether, and with diethyl ether. Such experiments are under way.

Summary

The homogeneous unimolecular decomposition of mixtures of dimethyl and diethyl ether has been investigated. The efficiency of energy transfer between molecules of the two substances is zero (within the experimental error), in so far as the production of activated molecules is concerned. The rates of decomposition of the separate reactants are therefore additive, and they have no mutual activating effect.

Physical Chemistry Laboratory,
McGill University,
Montreal, Canada.

[1] H. A. Taylor: J. Phys. Chem., **33**, 1793 (1929); Steacie and Campbell: Proc. Roy. Soc., **128A**, 451 (1930).
[2] Steacie and Morton: Can J. Research, **4**, 582 (1931); Steacie and Reeve: unpublished.

THE BEHAVIOUR OF THE GLASS ELECTRODE IN AQUEOUS SOLUTIONS OF SODIUM AND BARIUM ACETATE

BY MALCOLM DOLE

Freundlich and Rona[1] first investigated the glass electrode in solutions whose ions were multi-valent. They showed that although the electrokinetic potential of the glass aqueous solution boundary was changed considerably by changing the valence of the positive ion in the solution, the thermodynamic potential did not change at all or only with a change of the hydrogen ion concentration. It seems of interest to extend this study of the effect of multi-valent ions upon the thermodynamic potential of the glass electrode to solutions of high alkalinity because in this pH range, the potentials are functions of the concentration of ions such as lithium or sodium ions in addition to the hydrogen ion.

The author has recently advanced the hypothesis[2] that the mobility of the ions across the glass aqueous solution boundary may be influenced by the Helmholtz double layer. Since the large errors in alkaline solutions have been shown by him to be due to the relative mobilities of the ions across the boundary, it was thought that a study of the glass electrode errors under different boundary conditions might indicate if any connection between the Helmholtz double layer and the mobilities across this layer existed or not. The glass electrode shows a marked difference of behaviour in solutions of univalent and bivalent ions. In Fig. 1 the errors of the glass electrode in 1 normal sodium solutions are plotted along with the errors in 1 normal barium solutions. The barium solution errors are nearly within the experimental errors of measurement in contrast to those for the sodium ions which are very large. This difference has been experimentally demonstrated by a number of investigators.[3] Now the question which may be asked is, are the low errors of the glass electrode in barium solutions due to a low mobility of the barium ion across the boundary or are they due to a change in the Helmholtz double layer

FIG. 1

Errors of the Glass Electrode
Top Curve 1.0 N Sodium Acetate
Bottom Curve 1.0 N Barium Acetate

[1] H. Freundlich and P. Rona: Sitzb. preuss. Akad. Wiss., 20, 397 (1920).

[2] M. Dole: J. Am. Chem. Soc., 53, 4260 (1931).

[3] K. Horovitz: Sitzb. Akad. Wiss. Wien., Abt. II a, 134, 335 (1925); W. S. Hughes: J. Chem. Soc., 1928, 491; M. Dole: J. Am. Chem. Soc., 53, 4260 (1931). The data plotted are taken from this paper.

caused by the double positive charge on the barium ion? To solve this problem it was decided to carry out experiments in mixed barium and sodium solutions. If the barium acted solely through its mobility across the boundary, one would expect that the sodium ions would cause just as large an error in the presence of the barium as by themselves (except for a possible change in the activity of the sodium ion due to a change in the ionic strength), but if the effect of the barium ions is to change the mobility due to a change in the Helm-
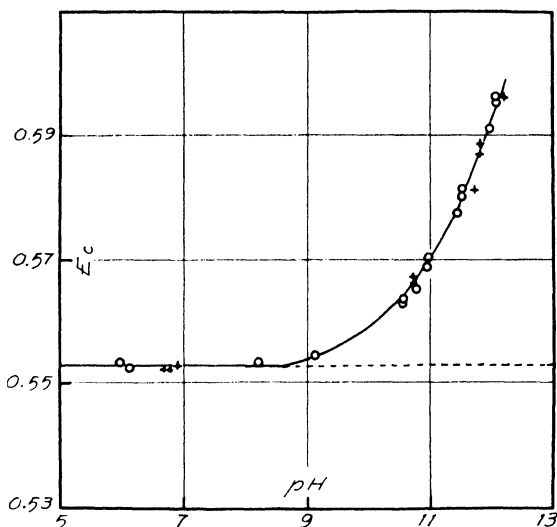
FIG. 2

Potential of the Glass Electrode in Sodium Acetate 0.5 N, circles; and in 0.5 N Sodium Acetate, 0.5 N Barium Acetate, crosses.

holtz double layer, one might expect the mobility of the sodium ion also to be changed and with this change in mobility a change in the error of the glass electrode.

Measurements were made of the following cells exactly in the manner already described;[4]

A. Hg | HgCl | Sat. KCl || Sodium or barium acetate solution | acetate buffer + sodium chloride || glass || AgCl | Ag

B. Hg | HgCl | Sat. KCl || Sodium or barium acetate solution | H₂ | Pt
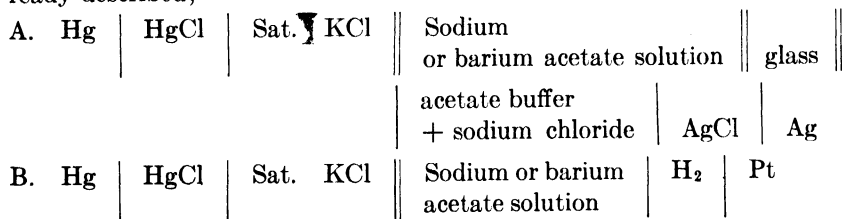
From measurements of cells A and B, the potential of the cell C may be obtained by difference.

C. Ag | AgCl | Acetate buffer + sodium chloride || glass || Sodium or barium acetate solution | H₂ | Pt
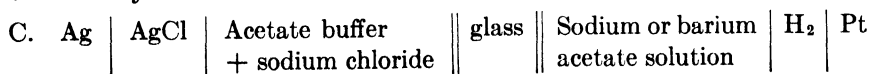
[4] Ref. (2).

Cell C should have a potential of 0.553 v. as long as the glass electrode shows no error; i.e., as long as it behaves as a perfect hydrogen electrode. The first experiments were made with 0.5 N NaAc solution, adding 0.5 N NaOH to increase the pH. Having obtained consistent results with this solution, a solution having the composition 0.5 N NaAc, 0.5 N BaAc$_2$ was then substituted and the measurements repeated. The results are recorded in Table 1 and are plotted in Fig. 2.

TABLE I

Potentials of the cell at 25°

Ag | AgCl | Acetate buffer + sodium chloride ‖ glass ‖ Sodium + barium acetate | H$_2$ | Pt

	0.5 N Na$^+$				0.5 N Na$^+$, 0.5 N Ba^{++}	
pH	Glass Electrode No.	ΔE		pH	Glass Electrode No.	ΔE
5.98	F-3	0.5536		6.68	F-34	0.5524
	F-4	.5526			F-35	.5522
8.23	F-27	.5538		6.79	F-34	.5530
9.16	F-27	.5549		10.73	F-34	.5672
10.59	F-3	.5639			F-35	.5662
	F-4	.5630		11.76	F-34	.5813
10.81	F-27	.5655		11.84	F-34	.5888
10.99	F-3	.5690			F-35	.5873
	F-4	.5704		12.22	F-34	.5965
11.48	F-27	.5773				
11.55	F-3	.5814				
	F-4	.5801				
12.03	F-27	.5911				
12.11	F-3	.5965				
	F-4	.5953				

From a study of the data and the figure it is evident that there is no significant difference between the two solutions; hence we can conclude that the barium ion has no influence upon the errors due to the sodium ions. If the barium ions do change the nature of the Helmholtz double layer by their presence, this change of the Helmholtz double layer has no influence on the mobility of the sodium ions across the glass aqueous solution boundary. In this connection it is interesting to point out that this experiment indicates that mixtures of barium and sodium ions could be analysed for their sodium content in much the same way that Urban and Steiner[5] analysed mixtures of sodium and potassium.

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[5] F. Urban and A. Steiner: J. Phys. Chem., **35**, 3058 (1931).

Experiments to be reported elsewhere have also been carried out in acid solutions in order to find out if the acid solution errors recently discovered by MacInnes and Belcher[6] are at all affected by change in valence of the ions present. These experiments likewise gave negative results.

Summary

The glass electrode behaves in mixtures of sodium and barium as if no barium were present. This indicates that the barium ion does not affect the mobility of ions across the glass aqueous solution interface due to any effect its double positive charge might have on the Helmholtz double layer.

Chemical Laboratory,
Northwestern University,
Evanston, Illinois.

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[6] D. A. MacInnes and Donald Belcher: J. Am. Chem. Soc., **53**, 3315 (1931).

ABSORPTION SPECTRA OF LIGNIN SOLUTIONS[1,2]

BY A. J. STAMM, JOS. SEMB AND E. E. HARRIS

Synopsis

The absorption spectra of a number of lignin solutions were determined, using the photographic method of Hilger and also a direct method in which the intensity of transmitted monochromatic light was measured with a thermopile. The results of the two methods agree satisfactorily. The hardwood lignins studied all gave characteristic absorption bands with maxima at 2740 to 2760 Å. The softwood lignins gave characteristic absorption bands with maxima at 2810 to 2850 Å. The different methods used for isolating lignin from wood had substantially no effect upon the absorption spectra. The lignin from partially chlorinated wood, or previously isolated lignin that was only partially chlorinated, when dissolved in a solution of sodium sulfite gave absorption bands that have extinction coefficients somewhat smaller than those of lignin solutions prepared from completely chlorinated wood or lignin. A thermal reaction product of cellulose, which is insoluble in 72 per cent sulfuric acid and which has been shown to have other characteristic chemical properties of lignin, gave an absorption band practically identical with that of lignin, except that the corresponding extinction coefficients were smaller.

Herzog and Hillmer[3] have shown that lignin solutions give a characteristic light absorption band in the ultraviolet. Cellulose and other carbohydrates, on the other hand, show no characteristic light absorption even in the short wave length ultraviolet.[4] These facts suggest that absorption spectra measurements should be of value in studying lignin, even in the presence of carbohydrate material. Further, absorption spectra measurements should aid not only in determining the molecular structure of lignin but also in determining the purity of lignins isolated by various processes. This preliminary paper deals primarily with the purity phase of the study.

The earlier absorption spectra measurements of Herzog and Hillmer[3] were made with the rather qualitative photographic method of Hartley-Baly. Their results show in a semiquantitative way the position of the absorption bands, but give only relative values for the extinction coefficients.

When the research reported here was under way, recent papers by Hägglund and Klingstedt[5] and Herzog and Hillmer[6] on the absorption spectra of

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[3] Herzog and Hillmer: Ber., 60B, 365 (1927); Z. physiol. Chem., 168, 115 (1927).

[4] Kwiecinski and Marchlewski: Bull. Inter. Acad. polonaise, (A) 1928, 271.

[5] Hägglund and Klingstedt: Z. physik. Chem., 152A, 295 (1931).

[6] Herzog and Hillmer: Ber., 64B, 1288 (1931); Papier Fabrikant, Fest und Ausland Heft, 1931, 40.

lignin were brought to the authors' attention. The results obtained by these investigators, using the photographic method of Henri which is more accurate than that of Hartley-Baly, are summarized in Table II for comparison with the results obtained in this investigation.

Experimental Methods

The absorption spectra measurements were made by two different methods, that of Hilger[7] and also a direct light-absorption one. A double cell, made by cementing matched quartz windows over two holes 1.0 cm. in diameter and 1.8 cm. apart that were drilled in a piece of plate glass 0.927 cm. thick, was used in both methods. A small slot, ground on one surface of the plate glass at the top of each hole and extending beyond the quartz plates, served in filling the cells. The spectrophotometer, which was of the Cornu prism type, gave a dispersion of 4 cm. over the range in wave length of 2500 to 2900 Å. An iron arc was used as the source of illumination.

Slight variations in the intensity of the light source have no effect upon the results obtained by the Hilger method, since the photographs of the solution and of the solvent are taken simultaneously. Further, the effect of any slight light absorption by the solvent is eliminated because of the comparative nature of the method. Another advantage is that absolute values of the extinction coefficient are obtained. The formula for the calculation required is

$$\epsilon = \frac{f}{cd} \log \frac{S}{S_o} \qquad \qquad (1)$$

where ϵ is the extinction coefficient in grams per liter, c is the concentration in grams per liter, d is the depth of the cell in centimeters, f is the correction for photographic density, S_o is the angle of the sector wheel opening[7] for the solvent, and S is the angle for the solution. The method used to obtain f will be given later in this paper.

In the direct light-absorption method, light from a mercury vapor lamp was focused upon a constant-deviation quartz monochrometer consisting of two 30° prisms. The monochromatic light was in turn focused upon an 11-junction platinum-iridium thermopile. The thermopile was connected to a sensitive suspension galvanometer, the deflections of which were read on a glass scale at a distance of 3 meters. A galvanometer deflection of 1 cm. was produced by 19 ergs of energy. The thermopile was carefully protected from stray light effects and the electrical parts of the apparatus were all grounded. The holder built for the cell permitted bringing either the solvent or the solution part into proper alignment in front of the monochrometer slit by merely pulling or releasing a cord.

With the conditions under which the measurements were made the galvanometer deflections are directly proportional to the intensity of the immergent light. The absolute extinction coefficient for any wave length

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[7] Weigert: "Optische Methoden der Chemie," 230 (1927).

can be readily calculated by making the measurements alternately upon the solvent and the solution. Then

$$\epsilon = \frac{1}{cd} \log \frac{I_0}{I} \tag{2}$$

where I_0 is the intensity of the light beam after passing through the solvent, I is the intensity after passing through the solution, and the other symbols have the same significance as in equation (1). The transmissive power of the two parts of the double cell were found to differ by 2 per cent when measurements were made at several different wave lengths, using distilled water; the necessary corrections were made in the calculations. Depending upon the intensity of the respective spectral lines, the light of the different wave lengths at which measurements were made caused the galvanometer deflections, for the solvent, to range from 2 to 16 centimeters.

The direct light-absorption method gives absolute values of the extinction coefficient directly, while the Hilger method involves the correction f for photographic density. This proportionality factor was obtained by making measurements on the same solution by both methods and then determining the shift along the extinction coefficient axis that would make the two curves identical. For determination No. 1, Table I, f was found to be 0.532. This value was used in all of the following calculations on measurements made by the Hilger method.

Solutions studied

A 2 per cent solution of sodium sulfite was used as the solvent in a large number of the measurements. Baly and Bailey[8] have shown that these solutions cause an appreciable absorption of light below a wave length of 2800 Å. In this investigation a fresh 2 per cent solution of sodium sulfite gave complete absorption below 2550 Å. The sodium sulfite solutions undergo a change on standing even when kept in sealed flasks. After several days of standing they transmitted light down to 2320 Å. When the lignin solutions in sodium sulfite solution were made up several days before the measurements were made, the light-absorption effect of the solvent was found to be negligible above a wave length of 2500 Å. For this reason all of the lignin solutions in sodium sulfite solution that were investigated were several days old.

The lignin solutions were prepared directly from wood and also from isolated lignin. Those from wood were prepared by the Cross and Bevan method; 2 grams of wood were treated with chlorine and the lignin dissolved in 100 cc. of 2 per cent sodium sulfite solution or water. The solutions of isolated lignin were prepared by chlorinating 0.2 gram samples and then dissolving them in 50 cc. of sodium sulfite solution. The solution of isolated lignin in ethyl alcohol (determination No. 13, Table I) was prepared by extracting a sulfuric acid lignin with the alcohol in a Soxhlet extractor for two days. At the end of this time no more lignin went into solution. The isolated lignins were prepared according to recognized procedures. The time

[8] Baly and Bailey: J. Chem. Soc., **121**, 1813 (1922).

and the temperature of treatment with 72 per cent sulfuric acid, for the sulfuric acid lignins, are given in parentheses in Table I. The sulfite liquor was obtained from a normal sulfite digestion in which lime was used as the base.

The thermal reaction product of cellulose was obtained by heating maple Cross and Bevan cellulose containing 5.25 per cent of moisture in a sealed glass tube to 138° C. for 8 days. The brown product thus obtained gave, upon chlorination and treatment with sodium sulfite solution, a solution that showed many of the chemical characteristics of lignin.[9] Treating the heated cellulose with 72 per cent sulfuric acid caused an appreciable residue corresponding to that of lignin. This residue after chlorination is soluble in sodium sulfite solution, in acetic acid or glycol containing a small amount of hydrochloric acid, and in strong alkali. The solution used for the absorption measurements was obtained by chlorinating the 72 per cent sulfuric acid residue and dissolving the result in sodium sulfite solution. Only one chlorination was made, whereas several are required for complete solution of the lignin-like material. The results should thus be comparable with the partially chlorinated lignins.

The total concentration of organic matter was taken to represent the lignin concentration, except for determination No. 1 of Table I, for which the pentosan content (15.3 per cent) was deducted. This inclusion of the pentosan content with the lignin concentration makes the extinction coefficients from 6 to 10 per cent too low for determinations Nos. 3, 4, 5, and 6.

Discussion of Results and Conclusions

Figs. 1 and 2 give the absorption spectra curves for all of the measurements and Table I summarizes the measurements. The numbers on the curves correspond to the numbers of the determinations given in Table I.

The results for determinations Nos. 1 and 2 showed that the presence of pentosans in the solution had no effect upon either the position of the absorption band or the values of the extinction coefficients when the concentration of pentosans present is subtracted from the total concentration in making the calculations. This not only substantiates the findings that carbohydrates show no appreciable light absorption but also indicates that the dilute alkali treatment used to extract the pentosans has no effect upon the characteristic light-absorbing part of the lignin molecule.

The light-absorption curves for chlorinated lignin dissolved in sodium sulfite solution and dissolved in water are practically identical above a wave length of 2500 Å (determinations Nos. 4 and 5). Below this wave length the absorption of the sulfite solution, even though several days old, is appreciable, as shown in the foregoing.

Lignin solutions prepared from only partially chlorinated wood or lignin (determinations Nos. 3 and 7) give the same absorption band as the solutions prepared from the completely chlorinated material (determinations Nos. 4

[9] Hawley and Wiertelak: Ind. Eng. Chem., **23**, 184 (1931); Hawley and Harris, Paper presented before the Division of Cellulose Chemistry at the eighty-first meeting of the American Chemical Society and to be published soon.

A. J. STAMM, JOS. SEMB, AND E. E. HARRIS
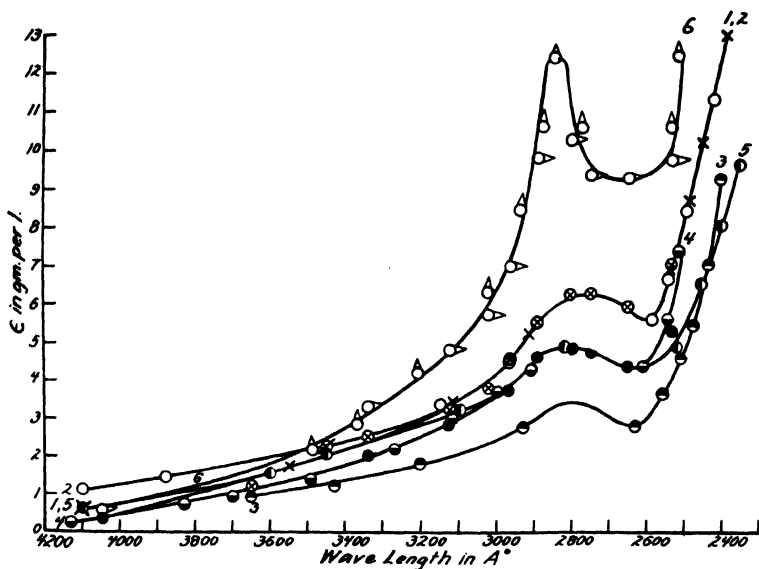
FIG. 1

✕ 1. Hilger method	◓ 4. Hilger method
⊗ 1. Direct method	● 4. Hilger method
○ 2. Hilger method	◐ 5. Hilger method
◕ 3. Hilger method	◌ 6. Hilger method

○▷ 6. Direct method
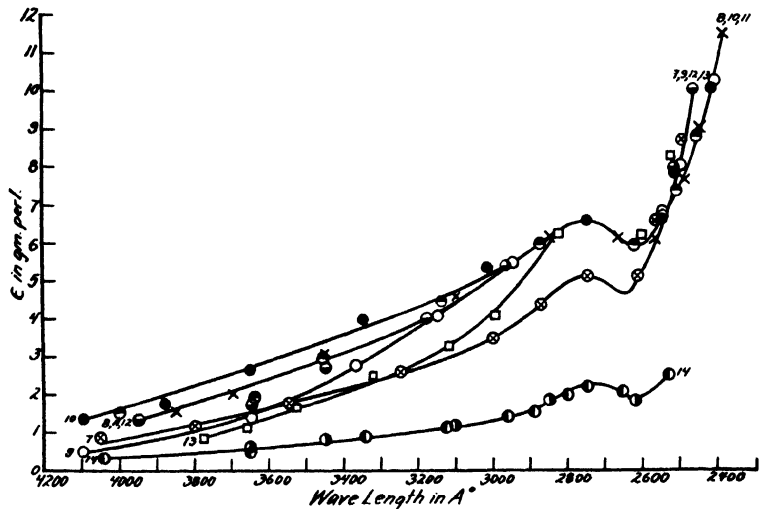
FIG. 2

⊗ 7. Hilger method	◓ 11. Hilger method
✕ 8. Hilger method	◒ 12. Hilger method
○ 9. Hilger method	□ 13. Hilger method
● 10. Hilger method	◑ 14. Hilger method

◐ 14. Direct method

Table 1 carries the key to the determination numbers.

and 8) except that the corresponding extinction coefficients are smaller. This is similar to the effect reported by Hägglund and Klingstedt.[5] They found that amyl lignin prepared by partial solution in amyl alcohol containing 1 per cent hydrochloric acid gave smaller extinction coefficients than when the lignin was almost completely dissolved (Table II). This shift in the extinction coefficients they reported can be due to differences in solubility of the constituents of a mixture made up either of molecules of the same molecular weight but containing different proportions of the characteristic absorbing group, or of different molecular-weight species each containing the same characteristic group. Further study will be necessary to determine the facts. The measurements indicate strongly, however, that lignin is not a simple monomolecular substance.

The measurements show a definite displacement in the absorption-band maxima between hardwoods and softwoods. This same displacement was noted by Hägglund and Klingstedt[5] and by Herzog and Hillmer[6] (Table II). The maxima for hardwoods were found to be within the narrow range of 2740 to 2760 Å in all of the investigations. Softwoods, on the other hand, showed a range for the position of the maxima from 2800 to 2870 Å. This variation is surprisingly small for measurements made upon such widely different lignin preparations as those studied by different investigators, using different experimental methods. The exact nature of this difference between lignin preparations obtained from the two types of wood is still unknown. Differences in the chemical reactions and in the methoxyl content have been recognized for years, but the shift in the absorption spectra band can hardly be due to differences in the number of methoxyl side chains. The difference must be due to a variation in the characteristic absorption group.

Isolated lignins prepared by several modifications of the sulfuric acid method, by the Willstätter hydrochloric acid method, and by the Freudenberg cuprammonium method all gave practically identical absorption bands, with the extinction coefficients differing appreciably only for the longer wave lengths. These results show that the lignins prepared by these different methods do not differ in the characteristic absorbing groups. Differences in the methoxyl content that do exist among the different lignin preparations can affect the results only in so far as they shift the extinction coefficients because of differences in molecular weight.

A solution of isolated lignin prepared by complete extraction with alcohol in a Soxhlet extractor showed an absorption band virtually identical with that obtained by chlorinating and dissolving the same lignin preparation in sodium sulfite solution. Differences in the extinction coefficients occurred only in the longer wave lengths.

The measurements on the calcium salt of lignin sulfonic acid, the only solution studied that was also studied by either of the other groups of investigators, gave results in good agreement with those obtained by Hägglund and Klingstedt[5] (Tables I and II). In both investigations these were the sharpest maxima obtained, a fact that may have some significance.

<div align="center">

TABLE I

Absorption Spectra of Lignin Solutions

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Determination No.	Species	Nature of lignin solution	Solvent	Concentration	Method of measurement	Position of maximum	ε at maximum	Position of minimum
				Grams per liter		Å	Grams per liter	Å
1	Sugar maple	Cross and Bevan; complete chlorination	2 per cent Na₂SO₃	0.125	Direct	2760	6.3	2610
				.0669	Hilger	2760	6.3	2610
2	"	Cross and Bevan; complete chlorination (pentosans extracted from wood)	2 per cent Na₂SO₃	.102	"	2760	6.3	2610
3	White spruce	Cross and Bevan; chlorinated 1 minute in desiccator filled with Cl₂.	2 per cent Na₂SO₃	.1265	"	2810	3.4	2640
4	"	Cross and Bevan; complete chlorination	2 per cent Na₂SO₃	.157	Direct	2820	4.8	2630
				.157	Hilger	2820	4.8	2630
5	"	"	Water	.0717	"	2820	4.8	2630
6	Spruce	Sulphite liquor	CaSO₃ solution	.1095	Direct	2850	12.3	2650
				.0547	Hilger	2850	12.3	2650
7	Sugar maple	H₂SO₄ lignin (16-hour treatment at 10°C.); chlorinated 1 minute in desiccator filled with Cl₂	2 per cent Na₂SO₃	.133	"	2750	5.1	2640

TABLE I (Continued)

Adsorption Spectra of Lignin Solutions

Determination No.	Species	Nature of lignin solution	Solvent	Concentration	Method of measurement	Position of maximum	ϵ at maximum	Position of minimum
				Grams per liter		Å	Grams per liter	Å
8	Sugar maple	H_2SO_4 lignin (16-hour treatment at 10°C.); complete chlorination	2 per cent Na_2SO_3	.0756	Hilger	2760	6.7	2610
9	"	H_2SO_4 lignin (3-hour treatment at room temperature); complete chlorination	2 per cent Na_2SO_3	.0834	"	2760	6.7	2610
10	"	H_2SO_4 lignin (16-hour treatment at room temperature); complete chlorination	2 per cent Na_2SO_3	.0854	"	2760	6.7	2610
11	"	HCl lignin; complete chlorination	2 per cent Na_2SO_3	.0768	"	2760	6.7	2610
12	"	$CuNH_3$ lignin; complete chlorination	2 per cent Na_2SO_3	.0848	"	2760	6.7	2610
13	"	H_2SO_4 lignin (16-hour treatment at room temperature); complete extraction in Soxhlet	Ethyl alcohol	.1375	"	2760	6.7	2610
14	"	Synthetic lignin (Cross and Bevan cellulose heated eight days at 138°C in a sealed tube); partial chlorination	2 per cent Na_2SO_3	.231 .180	Direct Hilger	2740 2740	2.2 2.2	2620 2620

TABLE II

Absorption Spectra of Lignin Solutions by Other Investigators using the Method of Henri

Investigators	Species	Nature of lignin solution	Solvent	Position of maximum	ε at maximum	Position of minimum
				Å	Grams per liter	Å
Hägglund and Klingstedt	Spruce	Amyl lignin	Alcohol	2840	18.8	2575
"	Pine	"	"	2830	18.8	2570
"	Birch	"	"	2760	12.5	2590
"	Beech	"	"	2755	12.5	2590
"	Spruce	Amyl lignin, 10-minute extraction	"	2810	14.9	2560
"	"	Amyl lignin, 30-minute extraction	"	2810	15.9	2580
"	"	Amyl lignin, 6 hour extraction	" .	2810	21.1	2600
"	Birch	Amyl lignin, 10-minute extraction	"	2750	8.0	2585
"	"	Amyl lignin, 30-minute extraction	"	2740	9.4	2695
"	"	Amyl lignin, 6-hour extraction	"	2750	13.9	2610
"	Spruce	Amyl lignin	Dilute alkali	2870	17.5	2680
"	"	Metholated amyl lignin	Alcohol	2830	22.7	2600
"	Beech	"	"	2755	14.0	2610
Herzog and Hillmer	Spruce	Glycol lignin	Dilute alkali	2820	19.5	2630
"	Beech	Ethyl lignin	Alcohol	2750	5.4	2630

Table II (Continued)

Absorption Spectra of Lignin Solutions by Other Investigators using the Method of Henri

Investigators	Species	Nature of lignin solution	Solvent	Position of maximum Å	ε at maximum Grams per liter	Position of minimum Å
Hägglund and Klingstedt	Spruce	Ethyl lignin	Alcohol	2830	18.9	2575
"	"	Methyl lignin	"	2815	19.1	2585
"	"	Calcium salt of lignin sulfonic acid	Water	2830	13.8	2630
"	Birch	Calcium salt of lignin sulfonic acid	"	2760	11.4	2610
"	Spruce	Lignin sulfonic acid	Alcohol	2840	13.8	2640
Herzog and Hillmer	"	"	Water	2800	6.5	2630
"	Basswood	"	"	2740	4.1	2610
"	Rye straw	"	"	2780	3.8	2590
"	Pine	Alkali lignin	Alcohol	2800	21.4	2700
"	Basswood	"	"	2740	20.0	2590
"	Rye straw	"	"	2760	20.4	2590
"	Jute	"	"	2750	9.8	2620
"	Flax	Pectin lignin	"	2790	19.1	2600
"		Polymer of coniferol alcohol[1]	"	2780	25.0	2540

[1] For values on related aromatic compounds see Herzog and Hillmer, reference No. 6 in the present report.

The thermal-reaction product of cellulose that shows a number of chemical characteristics of lignin also gave an absorption band similar to that of lignin except that the extinction coefficients were smaller. The fact that this solution corresponded to a first fraction may account in part for the low extinction coefficient. The material, however, may consist of lignin together with an impurity that has either a slight or no absorption band, or the material may have the characteristic light-absorption band of lignin although necessarily having then a different molecular weight. The similarity of this synthetic product to natural lignin is being investigated further.

Although Herzog and Hillmer[6] have shown the similarity in light absorption of lignin and certain aromatic organic compounds, notably coniferyl alcohol and its polymers, the structure of lignin has never been definitely proven to be aromatic. A hydro-aromatic structure, which can best account for what appears to be a thermal synthesis of lignin, has not been eliminated as a possibility. Further investigation will be necessary for the drawing of definite conclusions.

THE CONDUCTANCE OF SOME SODIUM OLEATE SOLUTIONS IN RELATION TO INTERFACIAL ADSORPTION.*

BY RALPH F. NICKERSON AND PAUL SEREX

Introduction

In a recent investigation Johlin[1] has found that the relative values of surface tension of sodium oleate solutions between concentrations .0019 N and .059 N are much greater than those obtained by other investigators. Leeten[2] and Dennhardt[3] studied the conductivity of these solutions and reached the conclusion that the hydrolysis constant of sodium oleate is comparatively small. Hahne[4] studied the effect of benzene on the properties of the soap in aqueous solution, but the magnitude of the interface benzene/sodium oleate was unknown. The present investigation was undertaken for the purpose of redetermining the conductances of sodium oleate solutions in the range of concentrations stated, to compare the results with surface tension data, and to measure the relative interfacial adsorption between these solutions and various oils, in order that the function of the interface in emulsification of oil-in-aqueous sodium oleate solution might be more clearly defined.

Apparatus and Materials

The conductivity bridge was essentially the same as that described by Hall and Adams[5] except that a two-stage audio frequency amplifier was interposed between the bridge output and the head phones. The alternating current used had a frequency of 1000 cycles/sec.

The bridge circuit was calibrated according to the method suggested by Wark.[6]

The procedure described by Popoff[7] was followed in the preparation of the platinum black surfaces on the electrodes of the conductivity cell. The cell constant was about 0.3595. (Subject to the calibration curve of Wark's method.)

"Equilibrium" water with a specific conductance of about $.9 \times 10^{-6}$ mhos was used throughout the investigation.

Kahlbaum's "Purest" sodium oleate was recrystallized twice from absolute alcohol, and dried in a vacuum oven. The purified product was used to make a stock solution from which various concentrations were obtained by dilution.

* Condensed from the thesis submitted by Ralph F. Nickerson at Massachusetts State College, 1932, in partial fulfillment of the requirements for the degree of Master of Science.

[1] Johlin: J. Biol. Chem., **84**, 534 (1929).

[2] Leeten: Z. deut. Öl-Fett-Ind., **43**, 50, 65, 81 (1923).

[3] Dennhardt: "Handbuch der Chemie u. Tech. der le Öu. Fette." Goldschmidt, **3**, 417 (1910).

[4] Hahne: Z. deut. Öl-Fett-Ind., **45**, 245-8, 263-64, 274-76, 289-90, 308-10 (1925).

[5] Hall and Adams: J. Am. Chem. Soc., **41**, 1515-25 (1919).

[6] Wark: J. Phys. Chem., **34**, 885-6 (1930).

[7] Popoff: "Quantitative Analysis," 2d Ed., 450 (1927).

Benzene, toluene and carbon tetrachloride were high grade, obtained from the Eastman Kodak Company. Meta-xylene, hexane and heptane were technical grade from the same company.

Experimental

Conductivities of the several concentrations of sodium oleate were obtained by placing the solutions in the cell and allowing them to stand in the thermostat at 25°C for half an hour before measurements were taken. Aliquots were transferred carefully to prevent frothing. Contamination by CO_2 was minimized as much as possible. The data are presented in Table I.
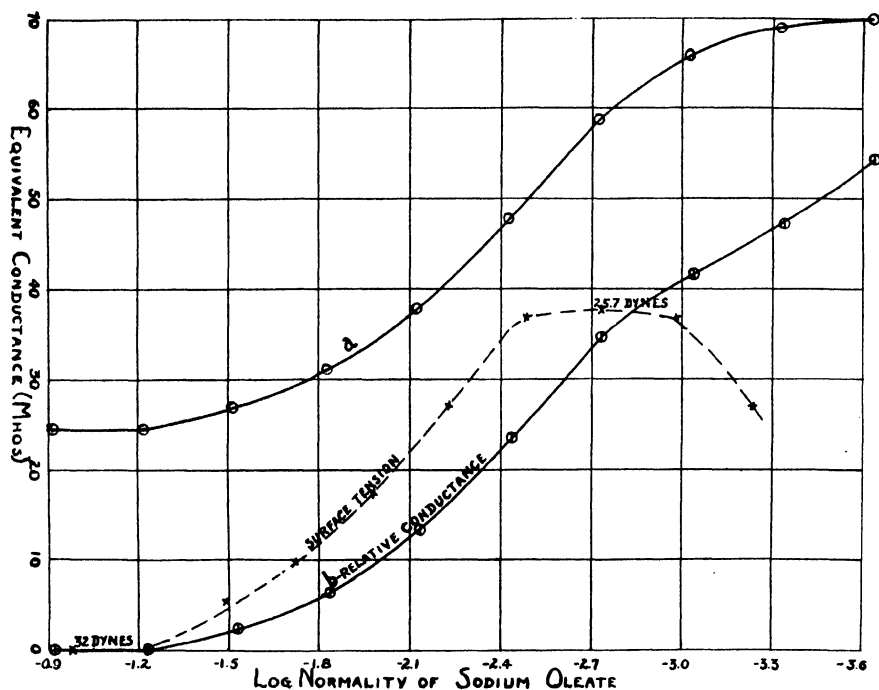
FIG. 1

The variation of equivalent conductance (a) and relative conductance (b) with logarithm of concentration of sodium oleate. The dotted line is Johlin's surface tension data.

TABLE I

Equivalent Conductance of Sodium Oleate at 25°C

Normality Sodium Oleate	Equivalent Conductance (Mhos) at 25°C	Normality Sodium Oleate	Equivalent Conductance (Mhos) at 25°C
H_2O	$.83 \times 10^{-6}$	H_2O	$.83 \times 10^{-6}$
.1216	24.75	.0019	58.65
.0608	24.47	.00095	66.00
.0304	26.87	.00048	69.03
.0152	31.05	.00024	69.90
.0076	37.88	.00024 (13 hrs. later)	72.20
.0038	47.80		

The curve (Fig. 1-a) represents graphically the conductivity-log. concentration relationship. A decided break in the trend of the curve may be seen at about .002 N. Leeten fails to point out this "break" although his data show it.

To eliminate the possibility that the change of trend of the conductance curve was due to the less highly conducting salt, Na_2CO_3, which could result from the interaction of NaOH, a consequence of the hydrolysis of sodium oleate, and the CO_2 of the "equilibrium" water, conductances of sodium oleate and NaOH of the various concentrations were determined simultaneously on the same water. Subtraction of the specific conductance of the NaOH solu-
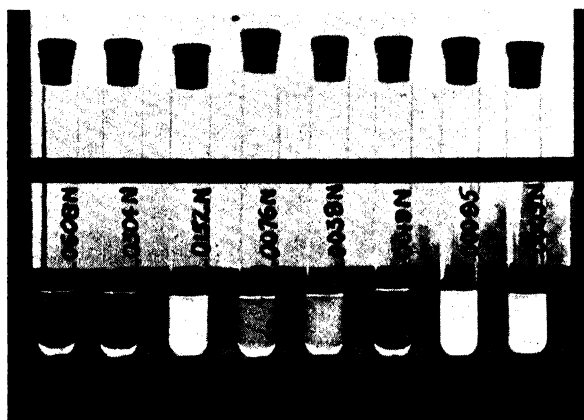
FIG. 2
The effect of dilution on the appearance of sodium oleate solutions. Photograph taken nine days after the dilutions were made.

tion from the corresponding figure for the sodium oleate solution gave a curve which showed the same effect (Fig. 1-b). The curve (Fig. 1-b) was taken, therefore, as the graphical representation of pure *increases* of mobility and hydrolysis with dilution.

An intense turbidity developed almost immediately in solutions of concentrations less than .002 N, but very gradually and much fainter in concentrations greater than .002 N. The photograph (Fig. 2) clearly illustrates this phenomenon. The conductances of the highly turbid solutions fall in the "break" of the conductance-log. concentration curve.

A small quantity of dilute alkali solution quickly removed this turbidity. Solutions of concentration .002 N or greater produced stable foams when shaken, whereas concentrations less than .002 N did not.

A number of investigators have shown that the minimum surface tension of aqueous sodium oleate solutions corresponds to about .002 N.

Discussion

From the photograph (Fig. 2) and the conductance-log. concentration relationship (Fig. 1) together with Johlin's surface tension data (Fig. 1) which have been plotted for comparison it is evident, first, that surface tension de-

creases as conductance increases from a .059 N solution down to a concentration of .002 N; second, that both surface tension and conductance are constant above .059 N at least as high as .120 N; and third, that the appearance of an intense turbidity is coincident with abrupt changes in the trends of the conductance and surface tension curves. In solutions of concentration .02 N or greater the colloidal material flocculates and settles on standing. McBain[1] and his students find that "acid soap" results from hydrolysis. If increasing conductance be taken as a criterion of increasing hydrolysis it is apparent that surface tension decreases as hydrolysis proceeds between the limits .059 N and .002 N. The lowering of the surface tension over this interval must be attributed to the hydrolytically formed "acid sodium oleate" and increases of mobility of the conducting particles.

Adsorption at the Oil/Sodium Oleate Interface

In order to inquire into the mechanism of oil-in-water stabilization by sodium oleate, the following studies were carried out on sodium oleate solutions with varying interfacial conditions.

Experimental

The first series of experiments consisted of varying the concentration of the sodium oleate solution under constant interfacial conditions. For each of the various concentrations of sodium oleate the procedure was as follows: 10 cc. of the solution were placed in the conductivity cell and permitted to reach surface and thermal equilibrium at 25°C. The conductance of the solution was then determined. A 2 cc. portion of benzene was then carefully layered on the surface of the solution in the cell and after 23 hours the conductance redeter-

TABLE II

The Effect of a Surface Layer of Benzene on the Conductance of Sodium Oleate in 23 Hours at 25°C

Concentration	Equivalent Conductance	Equivalent Conductance after 23 hours	Δ Equivalent Conductance
.0608 N	26.89	27.29	.40
.0304 "	28.85	30.07	1.22
.0152 "	32.85	37.22	4.37
.0076 "	38.81	53.53	14.72
.0038 "	49.16	73.14	23.98
.0019 "	59.16	82.99	23.83
.0010 "	73.21	86.95	13.74
.0005 "	73.48	87.37	13.89

Controls

.005 N NaOH	235	229.5	−2%
.001 "	216	210.	−3
.0005 "	205	197.5	−3.5

[1] McBain: J. Soc. Chem. Ind., Jubilee Number, 1931, 238.

mined.   Controls consisting of benzene layered on dilute solutions of sodium hydroxide were determined in the same way.   The data obtained are presented in Table II.

These data have been plotted (Fig. 3) together with the surface tension measurements of Johlin for reference.

It was observed, also, that the layer of benzene caused the colloidal turbidity to dissolve in a few hours with the result that the aqueous layer was clear and transparent.

The second series of experiments consisted of varying the oil while the other conditions were kept constant.   The procedure was the same as that just outlined except that 10 cc. portions of a .0118 N sodium oleate solution
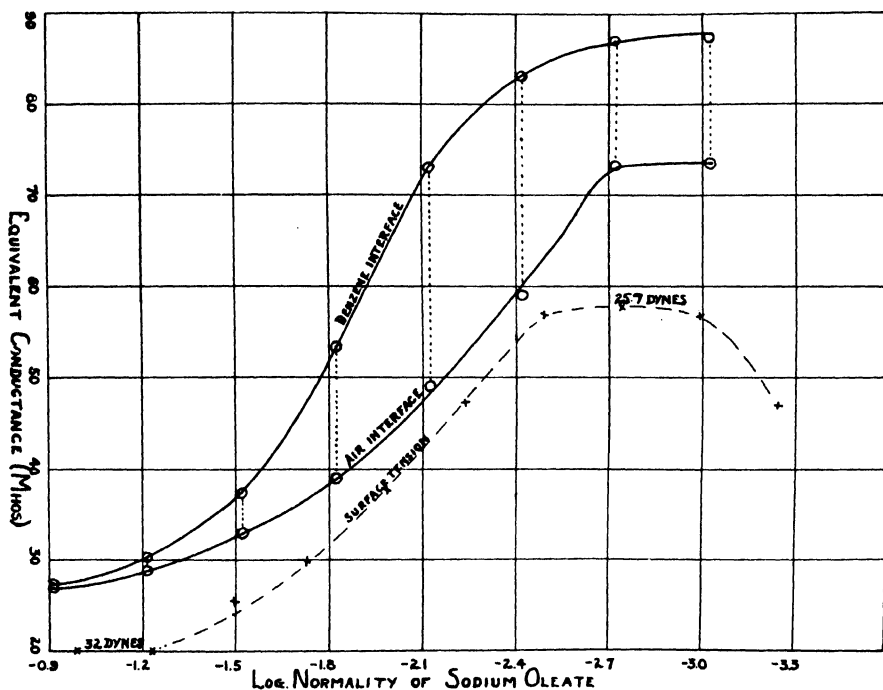
FIG. 3
A diagram showing the increases of equivalent conductance of various concentrations of sodium oleate in contact with benzene for 23 hours.   The surface tension curve after Johlin.

were used in each case, and 2 cc. portions of different oils were layered on the surface.   The rate of change of conductance was obtained by noting the time.   Oil-NaOH controls were determined also.   The experimental error, as manifested by the controls, is taken into consideration in the graphical representation of this data (Fig. 4).

The third series of experiments was concerned with a varying interfacial area, while the other conditions were held constant.   Pyrex vessels, which gave different areas of the benzene/solution interface with the same volumes of sodium oleate solution and benzene, were set up in the thermostat.   A 25 cc. aliquot of the same sodium oleate solution was placed in each container.   A

25 cc. portion of benzene was then layered on the interface in each vessel. After 30 hours an aliquot from the aqueous layer of each vessel was transferred to the conductivity cell and the measurement taken. Toluene, carbon tetrachloride, and m-xylene were determined in the same way. The data are plotted (Fig. 5).

Discussion

A layer of benzene on sodium oleate solutions whose concentrations varied from .059 N to .001 N brought about increases in the conductances of these solutions. In the case of concentrations .002 N or greater the more turbid the solution, the smaller was the increase of conductance. Under the conditions
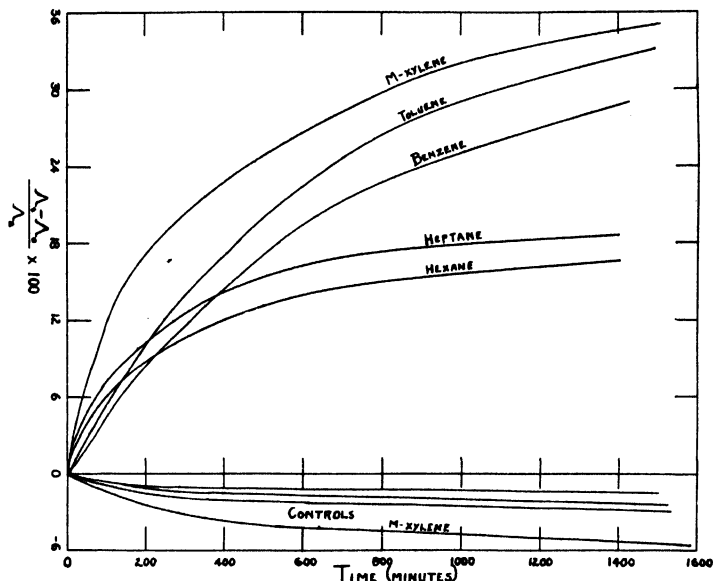
FIG. 4

The rate of percentage increase of conductance of .0118 N sodium oleate solution due to surface layers of various oils. The controls consist of the same oils on dilute sodium hydroxide.

of the experiments the increments of conductance were negligible in concentrations greater than .059 N. The experimental errors due to the diffusion of CO_2 through the benzene layer and its subsequent interaction with the NaOH resulting from the hydrolysis of sodium oleate, and to the distribution of impurities in the benzene layer between the two liquid phases, were negative with respect to the increments of conductance. The results with sodium oleate solutions are, therefore, probably slightly low.

The colloidal "acid sodium oleate" which was present as a finely divided white solid when the interface of the aqueous sodium oleate solution was in contact with its saturated vapor, went into solution when benzene was layered on the surface. This transition from a turbid to a clear solution was not observed when the concentration was less than .0005 N. The addition of a small quantity of dilute alkali had the same action on any of these solutions, namely, a clarification.

The areas of the vessels used in the surface variation experiments could not be measured with precision and the errors involved in transferring aliquots to the conductivity cell are certainly not negligible, but the data taken under the same conditions show that the conductance increases with larger and larger areas of contact oil/sodium oleate solution.

Conclusions

The presence of benzene on the surface of sodium oleate solutions under the conditions already mentioned brings about increases of conductance of these solutions. The shifts in conductance increase with time. The magnitude of
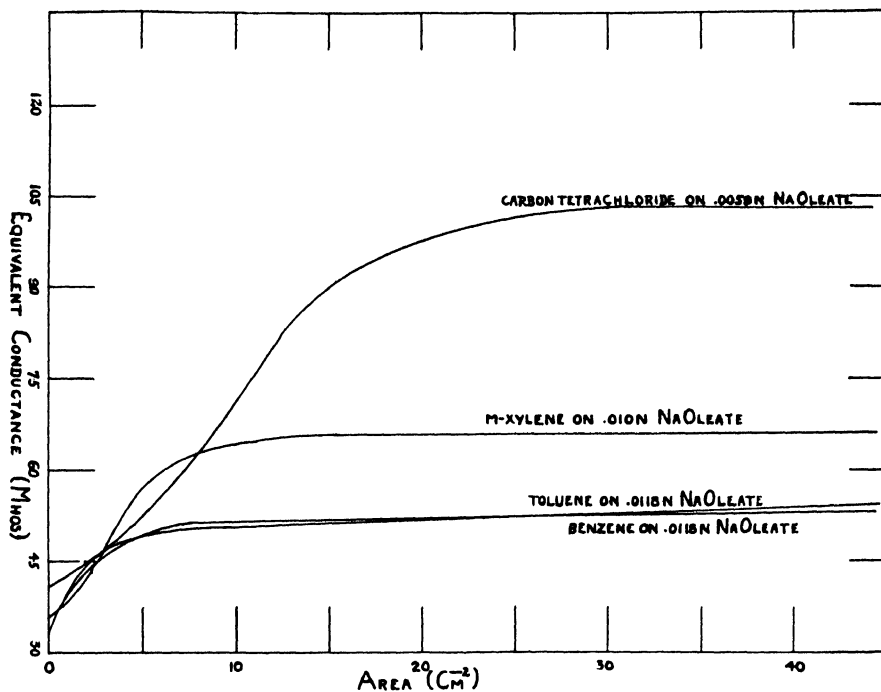
FIG. 5

The changes of equivalent conductance of sodium oleate solutions caused by varying the interfacial area between the oil and the solution.

the increment in any specific case is limited by the amount of "acid sodium oleate" which is present as a colloidal suspension in the solution when benzene is absent from the interface. As the conductance increases, the solution clears.

From the assumption that .002 N is the minimum concentration of sodium oleate for which the interface against air is saturated[1] and that all solutions of this soap of greater concentration than .002 N have saturated interfaces, it is evident that the surface activity of these sodium oleate solutions is determined to a great extent by the "acid sodium oleate" which results from hydrolysis of the neutral salt. The surface tension is a minimum at .002 N and

[1] Harkins, Davies and Clark: J. Am. Chem. Soc., **39**, 54 (1917).

the solution is clear (Fig. 2) which indicates a maximum concentration of the "acid sodium oleate" in the interface. The surface tension increases as hydrolysis decreases because the ratio of the *more water soluble* component sodium oleate to the less soluble "acid sodium oleate" in the surface becomes larger and larger until the surface becomes saturated with sodium oleate and the surface tension as well as the conductivity becomes constant.

The result of the presence of benzene in the interface is the displacement of sodium oleate from the interfacial film and the substitution[1] of "acid sodium oleate" which exists largely in colloidal suspension in the case of the solution/vapor interface. The exchange takes place until the colloidal excess becomes exhausted. The removal of the excess "acid sodium oleate" from the solution is followed by further hydrolysis of the sodium oleate which is recorded as increments of equivalent conductance (Fig. 3). A study of the changes in the equivalent conductance that take place as the interfacial area is increased (Fig. 5) leads to the conclusion that hydrolysis of the sodium oleate induced by the presence of the oil ceases when the concentration of alkali reaches a "suppressing value." Further adsorption must remove from the solution both sodium oleate and "acid sodium oleate."

The various oils used in this investigation show marked differences in the induction of hydrolysis (Fig. 4). Such differences may be interpreted as meaning that the interfacial energy between the oil and the sodium oleate solution determines the quantity of "acid sodium oleate" adsorbable and hence the concentration of alkali which is capable of suppressing further hydrolysis.

Increments of conductance of these sodium oleate solutions due to the influence of an oil layer on the interface indicate that the surface active material is in equilibrium with that dissolved in the main bulk of the solution. The "acid sodium oleate" is more highly adsorbed at the oil/solution interface than it is at the vapor/solution interface for the same solution of sodium oleate because its fugacity from the aqueous phase is determined by its solubility in the interface. The solubility in the interface, in turn, is conditioned by the interfacial energy.

In discussing the results of Briggs[2], Clayton[3] says: "This assumption may not be strictly true, as possibly the difficultly-soluble acid sodium oleate produced by hydrolysis may be a factor in emulsification." It is hoped that this investigation clarifies the action of "acid sodium oleate" in emulsoid systems.

Frothing is observed only in those solutions which have a saturated surface and an excess in colloidal suspension or as a crystalloidal precipitate. Stable foams may be obtained, therefore, on solutions in which there is an excess in equilibrium with the surface and the hydrolytic system.

Further investigations along this line are being carried on at this laboratory.

[1] Nonaka: J. Soc. Chem. Ind. Japan, **32**, 115-20 (1929) reaches essentially this conclusion from cataphoretic studies.

[1] Briggs: J. Phys. Chem., 19, 210-31 (1915).

[2] Clayton: "Theory of Emulsions," 2d Ed., 84 (1928).

Summary

1. At concentration .002 N sodium oleate shows an abrupt change in the trend of the concentration-conductivity relationship. This change of trend is coincident with minimum surface tension and loss of frothing power.

2. Surface tension of sodium oleate solutions varies inversely with hydrolysis between the limiting concentrations .059 N and .002 N.

3. More "acid sodium oleate" is adsorbed at the oil/solution interface than at the vapor/solution interface of the same sodium oleate solution.

4. Various oils have differing capacities to adsorb "acid sodium oleate."

5. The mechanism of the buffer action of sodium oleate in solution has been demonstrated.

6. The rôle of "acid sodium oleate" in emulsification has been much underated.

7. Frothing is attributed to a hydrolytic system in equilibrium with a saturated surface and an excess, colloidal, or colloidal and crystalloidal, depending on the concentration.

Goessmann Chemistry Laboratory,
Massachusetts State College,
Amherst, Mass.
February, 1932.

THE SYSTEM:—$CuSO_4$—$CoSO_4$—H_2O

BY H. D. CROCKFORD AND D. J. BRAWLEY

A search of the literature fails to reveal any data on the system: $CuSO_4$ — $CoSO_4$ — H_2O. In this paper are given the solubility data for the·o° and 25°C isotherms.

Experimental Procedure. CP grade of J. T. Baker Chemical Co. copper sulphate and cobalt sulphate were used. These were subjected to recrystallization before use. A series of bottles holding approximately 100 ml were

$CuSO_4$

Temperature 25°C

H_2O

$CoSO_4$
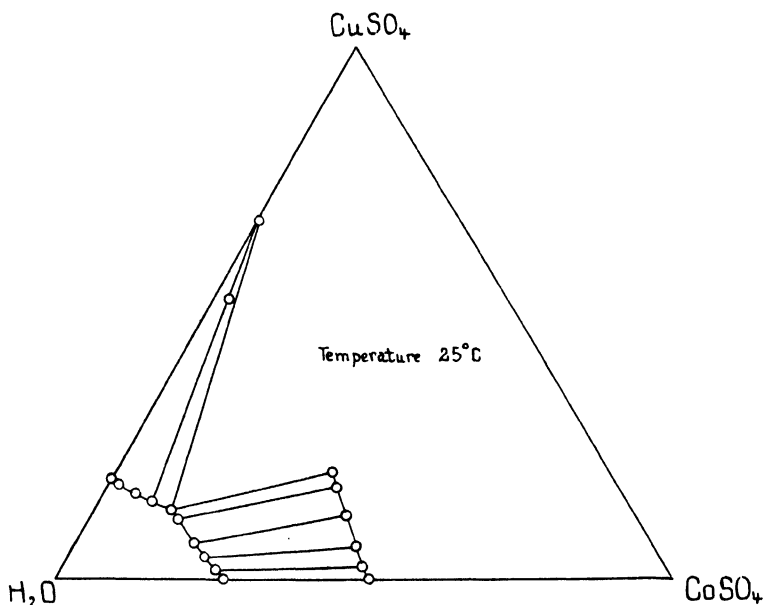
FIG. 1

prepared from saturated solutions of the sulphates. To some of the bottles an excess of one of the sulphates was added. In other cases saturation was carried out at a higher temperature than that of the isotherm to be determined and the solid phase was thus secured upon cooling. For the 25° isotherm the bottles were placed in a constant temperature bath constant to plus or minus .03°. For the zero isotherm the bottles were immersed in a container filled with crushed ice and water. This in turn was placed in a large refrigerator. A temperature very close to zero was thus secured. Equilibrium was rapid. This was especially true in the cases where supersaturated solutions were employed in the production of the solid phase. Only a few hours were necessary for equilibrium in these cases.

Both the copper and cobalt were determined electrolytically. After removal of the copper and before the removal of the cobalt the solutions were treated with ammonium hydroxide, sodium bisulphite, and ammonium sulphate according to the procedure of Dorothy H. Brophy.[1] Most excellent results were obtained with this procedure.
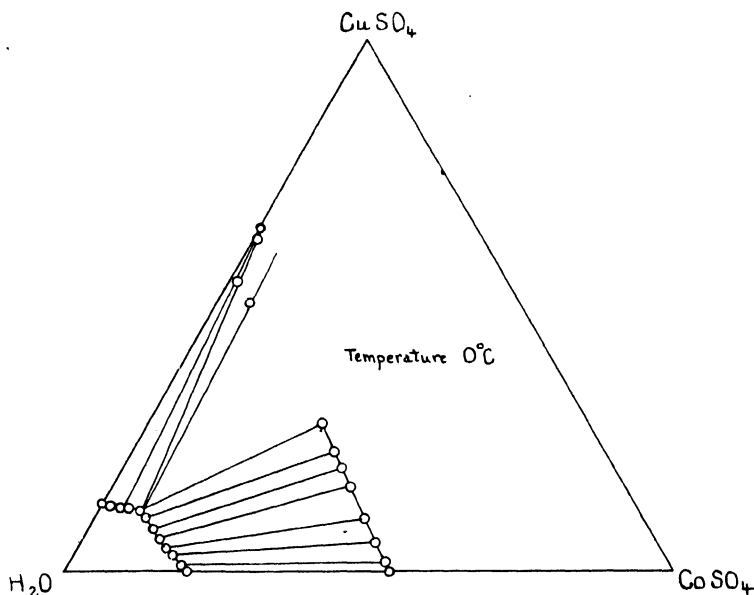
FIG. 2

TABLE I

$25°$ Isotherm

Bottle No.	Liquid		Solid		Composition of Solid
	Percent $CuSO_4$	Percent $CoSO_4$	Percent $CuSO_4$	Percent $CoSO_4$	
1	18.45	—	—	—	$CuSO_4.5H_2O$
2	18.18	1.14	—	—	"
3	16.66	5.07	—	—	"
4	14.68	9.70	51.82	2.58	"
5	12.91	13.80	63.30	trace	$CuSO_4.5H_2O$ and
5	"	"	19.88	35.77	Solid Solution
6	11.61	15.03	17.04	37.52	Solid Solution
7	7.45	18.55	13.04	41.88	"
8	3.71	23.25	6.66	48.20	"
9	1.76	25.24	2.99	51.78	"
10	—	27.16	—	—	$CoSO_4.7H_2O$

[1] Electrolytic Determination of Cobalt, Ind. Eng. Chem., Anal. Ed., **3**, 363 (1931).

In all cases the compositions of the solids were determined by removing some of the wet residue and freeing it as far as possible of the mother liquor before analysis. In the case of the solid solutions the crystals were usually large enough to make this procedure very easy.

Results. The data are given in Tables I and II and plotted in Figs. 1 and 2.

<div align="center">

TABLE II

0° Isotherm

</div>

Bottle No.	Liquid		Solid		Composition of solid
	Percent CuSO$_4$	Percent CoSO$_4$	Percent CuSO$_4$	Percent CoSO$_4$	
1	12.87	—	—	—	CuSO$_4$.5H$_2$O
2	12.78	1.00	—	—	"
3	12.55	2.80	51.53	0.80	"
4	12.33	4.05	—	—	"
5	11.90	5.93	62.19	0.69	CuSO$_4$.5H$_2$O and Solid Solution
5	"	"	49.46	4.39	"
6	12.01	5.96	27.92	26.73	"
7	9.53	7.89	21.99	28.00	Solid Solution
8	6.66	10.67	18.26	36.61	"
9	5.03	12.34	15.26	39.14	"
10	3.14	15.02	10.45	43.48	"
11	1.57	17.64	5.41	49.08	"
12	.59	19.08	1.38	53.57	"
13	—	19.82	—	—	CoSO$_4$.7H$_2$O

It is seen that the solid phases consist either of copper sulphate pentahydrate or a solid solution in which part of the cobalt in the cobalt sulphate heptahydrate is replaced by copper. The limiting solid solution in the 25° isotherm has the composition 19.88% CuSO$_4$ and 35.77% CoSO$_4$. In the 0° isotherm the composition is 27.92% CuSO$_4$ and 26.73 CoSO$_4$. The crystals of the solid solutions were always well-formed and showed the same crystalline shape as the cobalt sulphate heptahydrate. As the copper content increased an increasing bluish color appeared. The fact that cobalt and copper have so nearly the same atomic weight caused all the solid solutions to fall on the same straight line. The intersection of the solution curves was established by separation and analysis of the two phases present and by the fact that the further addition of copper sulphate pentahydrate to the bottles resulted in no change in composition of the liquid. It was not considered necessary to analyze all the solid phases.

Summary. The 0° and 25° isotherms for the system: CuSO$_4$ − CoSO$_4$ −H$_2$O have been determined. In both cases the solids consist of copper sulphate pentahydrate and a series of solid solutions in which copper partially replaces the cobalt in cobalt sulphate heptahydrate.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor.
Vol. XI. 24 × 17 cm; pp. xii + 909. London and New York: Longmans, Green and Co.,
1931. Price: $20.00.* This volume deals with tellurium, chromium, molybdenum, and
tungsten. It was published last year; but the review copy for the Journal of Physical
Chemistry either went astray, which is not likely, or was not sent until now.

"Tellurium occurs combined with gold, silver, bismuth, and many other metals. It is
rather a nuisance in certain auriferous districts where the gold and silver ores are unfit for
amalgamation, etc., because the telluride ores do not give up their gold to mercury, to
cyanide, or to chlorine; the ores also concentrate badly; they are difficult to roast on account
of their low melting-point and gold is lost during the removal of the tellurium. The telluride
ores are smelted either with lead or copper ores which act as a flux. Large amounts of
tellurium enter the copper matte. The mattes are then bessemerized, and the copper refined
by electrolysis. The copper contains not far from 0.04 per cent of tellurium. The slimes
contain most of the tellurium, antimony, caesium, and bismuth together with silver and
gold. The chief tellurium minerals are the tellurides; and the oxidized minerals are repre-
sented by tellurous acid, the tellurites and the tellurates," p. 2.

"Tellurium is insoluble in a normal solution of potassium hydroxide from which oxygen
is excluded. In a 10 N solution, however, it dissolves at 100° to form a red solution, from
which it separates on cooling or dilution. This points to the simultaneous presence of
positive and negative tellurium ions," p. 20. The author seems to have said too much or
too little.

"According to Auerbach, tellurium in accord with its metallic character dissolves in
pyrosulphuric acid as monatomic molecules, and, in coagulation, the colour changes from
red through violet to blue. . . . Fenaroli found that, as in the case of selenium, the oxidized
element does not colour glass; but, if reducing conditions are present, blue, brown, and red
glasses are obtained," p. 27.

"On account of some industrial applications, tellurium is beginning to acquire some
technical importance. It has a very limited application in the glass industry; it is used in
the preparation of organic dye-stuffs; in the manufacture of electrical equipment; high
resistance alloys and ultramarine; in the coloring of lithopone; the staining of silver; as a
delicate test of sterilization in bacteriology; and as a toning agent in photography. A com-
pound of tellurium has been used as an anti-knock constituent of motor fuels, and its use is
said to lead to greater efficiency. Remarkable properties are shown by the alloys of tellurium;
the tin alloys are extremely hard and have very great tensile strength; and the aluminium
alloys are very ductile. The silver alloys have been used. The element is poisonous, and is
fairly readily adsorbed—*e.g.* from gold dental stoppings. F. C. Mathers and J. Papish
used solutions of salts of tellurium for staining metals; C. Dickens used colloidal tellurium
as an insecticide, germicide, fungicide, and wood preservative," p. 30.

"According to F. W. Aston, the mass spectrum of tellurium gives lines corresponding with
isotopes of the the atomic weights 126, 128, and 130, the intensities of the latter two being
equal, and double that of the first. All the mass numbers of tellurium probably form
members of isobaric pairs," p. 35.

"Whilst β-sulphur retains two percent of tellurium in solid solutions, α-sulphur retains
only 0.5 percent; but the separation of the excess occurs only under the influence of light,"
p. 111.

"Müller and Soller said that chrome alum dissolved in N H_2SO_4 is not appreciably
oxidized to chromic acid by the use of an anode of smooth platinum; but a trace of lead in
the solution is precipitated on the anode as lead dioxide, and this brings about oxidation;
traces of chlorine also favour the oxidation," p. 131.

Nobody would guess from the author's account, p. 136, that Placet and Bonnet exhibited in Paris metallic chromium obtained by electrolyzing chromic acid, that the Germans questioned the possibility of obtaining chromium in this way, and that Carveth showed that it could be done.

"One of the most important applications of chromium is in the production of various alloys, principally ferrochromium alloys for the manufacture of special steels many of which contain about 2 per cent of chromium and a small proportion of other metals—*vide* the alloys of iron. The chrome-alloy steels are hard and tough. They are used in making armour-plate, armour-piercing projectiles, burglar-proof safes; tyres, axles, springs for railways and motor-cars, stamp-mill shoes, crusher jaws, the so-called rustless cutlery, stellite—an alloy containing chromium, cobalt, and molybdenum and tungsten—for high speed tools which require their cutting edge at temperatures approaching redness; nichrome—nickel, chromium, iron (60:14:15), a high-temperature resistance alloy; chromium-vanadium steel; chromium magnet steel; heat-resisting and acid-resisting steels; etc. Chromium plating as a protective coating for steel is much employed—*vide supra*, the electrodeposition of chromium. Perhaps the largest demand for chromium is in the form of chromite used as a refractory in certain parts of open-hearth and other furnaces. Chromium compounds are used in tanning certain leathers—chrome leathers; as a mordant for dyeing; it is used for impregnating wood, paper, etc., with chromic hydroxide; and in the preparation of filaments for incandescent lamps. Chromates are used for making gelatine insoluble—for a mixture of gelatine and potassium dichromate becomes insoluble when exposed to light—in color printing, block printing, heliography, photolithography, photozincography, etc. Chromium compounds are used in making safety matches; as antiseptics; in bleaching oils; in the purification of wood vinegar; as a component of certain galvanic cells; an oxidation agent in the preparation of some aniline dyes and in a number of analytical and chemical processes; as a catalytic agent in the preparation of sulphur trioxide (*q.v.*), and, according to H. W. Underwood, in the hydrogenation of organic compounds.

"Chromic oxide is employed as green pigments for paints—chrome-green, emerald-green, Cassel's green, etc.—and it may be associated with other substances—*e.g.* boric oxide, phosphoric oxide, zinc oxide, etc., to produce special tints, there are yellow chromates of lead, etc.—*e.g.* chrome yellow, lemon yellow, Paris yellow, royal yellow, etc.; red basic lead chromates—*e.g.* chrome-orange, chrome-vermilion, etc.; and brown, manganese chromate. Chromic oxide is employed in producing on-, in-, and underglaze green colours in enamel, pottery and glass manufacture; on-glaze yellows employed for on-glaze work, and in enameling are derived from lead chromate, the on-glaze reds and orange colours, from basic lead chromate. A crimson or pink colour for pottery decoration is based on the result of calcining stannic oxide with one or two percent of chromic oxide; for the coloration of alumina with chromium to form artificial rubies—*vide* alumina. C. J. Smithells described the manufacture of articles from chromium," p. 165.

On p. 177 the author says: "A very thin sublimate of chromic oxide is red, and this probably explains the colour of chrome-tin pink and of the ruby." This cannot be true unless the sublimate is an instable form. This statement is the more remarkable because the author cites Stillwell's experiments on the same page. One is also puzzled over the statements in regard to the dialysis of hydrous chromic oxide, p. 190. "It is hence calculated that the colloidal chromium particle consists of 1000 chromium atoms and carries 30 free charges. The number of chromic oxide molecules in a colloidal particle is about 240." This apparently means Cr_4O_6 for chromic oxide. "Wintgen and Rinde gave 580 for the number of chromic oxide molecules in a colloidal particle aged by boiling and 750000 for the case of an aged ferric oxide colloidal particle." The reviewer endorses the author's remark that "these numbers are of doubtful accuracy."

"Ferrous and magnesium chromites form solid solutions; so also do ferrous chromite and ferrous aluminate. There is also evidence that some ferrites and chromites form solid solutions," p. 202. Simon and Schmidt find Cr_5O_{13} and Cr_5O_{12} as definite chemical compounds between CrO_3 and Cr_2O_3, p. 206.

"Reese observed that, in the absence of a catalytic agent, a solution of chromic acid, alone or in the presence of 1-15 percent by volume of sulphuric acid, is not reduced by hydrogen below 50°; and only very slowly below 100°. After 116 hours exposure, 70 percent of hydrogen is oxidized; and at 156°, after 7 hours exposure, 11 percent of hydrogen is oxidized and much oxygen is evolved owing to the decomposition of the chromic acid. The oxidation is not dependent on the thermal decomposition of chromic acid because it occurs at a temperature below that at which oxygen is evolved," p. 229.

"When potassium dichromate is added in the theoretical quantity to a solution of stannous chloride in the absence of acid, brownish- and greenish-blue gelatinous masses are formed, which dissolve and form a clear deep olive-green solution when the whole of the dichromate has been added. These solutions appear red by transmitted light," p. 237. Berzelius observed that the lemon-yellow potassium chromate becomes bright red when heated, p. 253.

"According to Antony and Paoli, if excess alkali hydroxide be added to a solution containing a chromium and a manganese salt in the proportion Mn : 8 Cr, no precipitate is obtained, but the liquid is coloured emerald green and must be regarded as a colloidal solution of the hydroxides of chromium and manganese, since this behaviour is exhibited only when the salts are present in exactly the above ratio. [This last statement is of course an error.] Chromium being tervalent and having both an acid and a basic function, whilst the manganese is bivalent and decidedly metallic in its properties, it is inferred that they exist in this solution in the form of a salt, an electrolyte, which must be either a manganous chromite or polychromite," p. 308. Whatever else we may have, it is pretty certain that we do not have a dissolved manganous chromite or polychromite.

"The extraordinary confusion in the use of the terms plumbago, graphite, galena, and molybdena, which prevailed from the time of Aristotle, *circa* 350 B.C. to the 18th century, has been discussed in connection with carbon, and with galena. It is very difficult to pick out from the various references those which in all probability refer to molybdena. The term molybdaena is the Latinized form of the Greek μολύβδαινα, which is derived from μόλυβδος, lead. The term μολύβδαινα appears to have been applied by Aristotle, Dioscorides, Galen, Pliny, etc., to various things associated with lead—plummets, sinkers for fishing nets, bullets for catapults, etc.—to lead oxide obtained as a by-product in cupellation, and to natural lead ores," p. 484.

"Langmuir found that higher values for electron emission are obtained from filaments containing one to two percent thoria. With an ordinary thoriated filament, the thorium is present as the dioxide, and the electronic emission is the same as for tungsten alone; but if the temperature is raised above 2600°K., the thoria reacts with the tungsten to form thorium. This reaction was studied by C. J. Smithells. Langmuir found that the thoriated filament heated to 2600°K. gives the normal value for tungsten at 1500°K. since the thorium metal will have evaporated from the surface. It is therefore necessary after flashing the thoriated filament at 2800°K. for, say, 3 min. to lower the temperature to about 2000°K. to allow the thorium to diffuse to the surface from the interior. The emission at 1500°K. is then 100,000 times the value for tungsten alone—*vide supra*. If the temperature is kept below 1900°K., this high value is retained indefinitely, but it is destroyed above 2200°K. owing to the volatilization of the thorium," p. 712.

"The passivity of tungsten is due to oxide films, ranging in colour from brown, blue and green to yellow. The colours are pronounced and can be followed as the electrolysis proceeds. The films are independent of the dissolved cation or anion. They are due to the OH-ions reacting with the tungsten. The passivity is a function of the colour of the film, the colour varying with the amount of oxygen present. The passivity varies directly with the current, time and temperature, and inversely with the solubility of the film, the volume of electrolyte and the diffusion velocity. If the film dissolves as rapidly or more rapidly than it is formed, the tungsten will remain active. The films can be dissolved and the passivity destroyed. Solutions of potassium hydroxide and ammonia render passive tungsten active. Solutions of acids and salts make passive tungsten active if allowed to react for some time on it. Passive tungsten has been made active overnight in distilled water," p. 720.

"Some unique properties of tungsten have important industrial applications. It has a high density exceeding that of lead. Its melting-point is higher than that of any known metal; its tensile strength exceeds that of iron and nickel; it is paramagnetic and elastic so that it has been tried in electrical meters, and non-magnetizable watch-springs. It can be drawn into thinner wires than any other metal, and this fact, coupled with its chemical stability, offers possibilities in making suspensions for galvanometer needles, and cross-hairs for telescopes; and for thin wires in surgical operations in place of gold or silver wires. The greatest use of tungsten is in the preparation of iron or steel alloys, *e.g.* in the preparation of high-speed tool steels (*q.v.*). Tungsten forms alloys with many of the metals, and some of them have valuable properties although in many cases the cost of the alloy is out of proportion with its usefulness. The stellite alloy described by E. Haynes is an alloy of cobalt, chromium, and tungsten (75:20:5) with or without additions of other metals. It is a competitor for some high-speed cutting steels. J. T. Bottomley proposed an alloy called *platinoid*, composed of nickel, zinc, copper, and tungsten for conductivity wires. E. Weintraub patented an alloy with 40 to 80 percent of platinum for use in electrical contacts, jewelry, etc. *Partinium* is an alloy of aluminium and tungsten employed in automobile construction; *sideraphite*, an alloy of iron with nickel, copper, aluminium and tungsten; minargent, an alloy of copper, nickel, and tungsten; and *backford*, an alloy of copper, tin, and tungsten. F. A. Fahrenwald discussed the use of alloys of tungsten and molybdenum as substitutes for platinum for contact points in sparking coils, voltage regulators, and other electrical instruments. Gold-coated tungsten dental pins are also used in place of platinum," p. 735.

"A solid solution of copper tungstate in calcium tungstate is as luminous as scheelite; manganous tungstate acts like the copper salt. The tungstates of sodium, potassium, strontium, barium, and zinc; wolframite, ferberite, and the different tungstate bronzes, are not luminous when exposed to X-rays," p. 785.

"W. Ducca, and W. Löwinthal studied the action of luminophores—*e.g.* traces of manganese, copper, or bismuth salts—in enhancing the fluorescence of calcium tungstate when exposed to X-rays. The presence of 1/12,000th part of a bismuth salt gave the best results. The spectrum of the blue fluorescence of calcium tungstate containing a trace of a bismuth, manganese or copper salt shows feeble spectral bands in the blue violet; and when the tungstate contains a trace of a silver, gold, nickel, cadmium, antimony, or lead salt, the fluorescence is green. Calcium tungstate exhibits no thermoluminescence at room temperature; but when it is cooled to $-192°$, exposed to X-rays, and its temperature allowed to rise, it becomes luminescent, the glow is then extinguished, and as the temperature still continues to rise, a second luminescence appears. A small amount—say 0.1 gram.—shows only one thermoluminescence. The luminescence of calcium tungstate in cathode rays resembles that produced by X-rays," p. 785.

"R. Tronquoy found that powdered hübnerite is sulphur yellow, and with plates of decreasing thickness the colour changes in different directions are: *a*, dark red to brown to pale brick-red to olive-green; *b*, bright red to orange-red to greenish-yellow; and *c*, orange-red to bright yellow with a faint green tinge. Usually the higher the proportion of ferric oxide, the blacker the colour; but the black mineral from White Oaks has only 0.55 percent of ferrous oxide, whereas lighter coloured hübnerite may contain more ferrous oxide. The cause of the dark colour is unknown. Hübnerite may be pleochroic with *b* yellowish-brown, and *c* green. Ferberite is described by F. L. Hess as a black, opaque mineral which under the microscope may appear red by light transmitted through very thin edges—say 0.0001 to 0.0002 inch thick. Ferberite may occur coated with hydrated iron oxide, or be so intergrown with it that both the outside, and the parts exposed by fracture or cleavage may be brown. Some specimens are iridescent owing to thin films of oxide," p. 799.

Wilder D. Bancroft

	CO_2	CO	H_2	C_nH_{2n}	$2\ C_2H_4$
Berthelot and Gaudechon[1]	—	22.0	63.0	15.0*	—
Maquenne[2] 2 mm	2.2	11.0	42.6	30.0*	14.0**
" 100 mm	0.5	15.4	55.2	26.6*	2.3**
Poma and Nesti[3]	2.2	4.4	59.0	26.0***	9.0**
de Hemptinne[4]	2.0	22.0	25.0	48.0***	—
Löb[5]	1.0	5.5	68.2	22.1***	3.2

*C_2H_4
**C_2H_2 and C_2H_4
***CH_4 and C_2H_6

The experiments of Berthelot and Gaudechon[6] proved conclusively the formation of acetaldehyde.

"A quartz flask of 40 cc. filled with ethyl alcohol and cooled by means of water, was exposed for 4 hours at 6 cm. from the 110 volt lamp, functioning in a moderate fashion (3.6 amp. with 45 to 50 volts at the terminals). We then ascertained the reducing action on ammoniacal silver nitrate. The following reactions showed the presence of ethyl aldehyde: instantaneous recoloration with Schiff's reagent (fuchsine decolorized with sulfurous acid); yellow coloration after several minutes of boiling with concentrated soda and a little water; orange color upon contact with Hehner's reagent (water + a drop of phenol solution + concentrated H_2SO_4). All of these reactions tried on the original alcohol, before exposure, were negative."

Berthelot and Gaudechon, it will be remembered, stated that the essential feature of the photolysis of alcohols is an abundant evolution of hydrogen with the formation of the corresponding aldehyde. They obtained also some carbon monoxide and ethane.

Maquenne[7] detected aldehyde but concluded that the primary reaction in the discharge tube is the formation of ethylene.

"Ordinary alcohol (99.5) decomposes rapidly in the discharge tube. The evolved gas has a strong odor of aldehyde and acetylene. The gases were washed with water before analysis. . . . "Ethylene, relatively abundant when the pressure is very low, diminishes very rapidly; at a pressure of 100 mm. it is no longer found.

"It appears then that the alcohol, under the influence of the discharge, is separated into ethylene and water in an initial decomposition which is immediately followed by the secondary reaction. The ethane has a similar origin. It is in its turn decomposed little by little. The hydrogen then increases in a continuous fashion. Also in that case, it forms the polymerized products, of resinous appearance, which remain in solution in the undecomposed alcohol."

[1] Compt. rend., 151, 479 (1910).
[2] Bull., 40, 61 (1883).
[3] Gazz., 51, 86 (1921).
[4] Z. physik. Chem., 25, 288 (1898).
[5] Z. Elektrochemie, 12, 308 (1912).
[6] Compt. rend., 153, 383 (1911).
[7] Bull., 40, 61 (1883).

From the results of Poma and Nesti, reactions (a), (b), and (d) probably all took place, while in de Hemptinne's apparatus, reactions (a) and (d) occurred. Jackson and Northall-Laurie showed quite conclusively that reaction (a) occurred almost exclusively in their high-frequency ozonizer.

"Preliminary experiments and a number of analyses of the gaseous products showed that if these were allowed to accumulate by continuing the discharge for any length of time, the results obtained showed such variety as to be of little value for interpretation. If, however, the discharge were passed for a few seconds only, comparable results could be obtained. The vapours were under a pressure of about 100 mm. for methyl alcohol and 180 mm. for acetaldehyde and the discharge passed for from one to ten seconds. The products were then pumped out of the apparatus, separated from the vapours, and analyzed. Working in this way no solid or heavy liquid products were obtained, although these were observed if the discharge were continued for a long time.

"Several analyses were made of the gaseous products obtained in this way, and it was found that the shorter the time the current was allowed to pass, the more nearly did the composition of the products (from methyl alcohol) approximate to carbon monoxide and hydrogen, the volume of the hydrogen being very nearly double that of the carbon monoxide. By working with mere flashes of the discharge and pumping out the products after each flash, gases were obtained which, when freed from the vapour of methyl alcohol and traces of water, gave the following results as the mean of several determinations of the main products:

CO	H	CH_4	C_2H_2	C_2H_4
32.5	61.1	2.4	1.2	0.6

(percentage by volume)

"We conclude that the immediate action on the vapour of methyl alcohol of such oscillations as are obtained in high frequency discharge is represented by the simple change

$$CH_3OH = CO + 2H_2.$$"

Maquenne, and Poma and Nesti used somewhat the same kind of discharge and their results show a similarity. Reaction (a) giving $CO + H_2$ probably did not occur in Maquenne's apparatus and only slightly in Poma and Nesti's . Reaction (b) giving formaldehyde, occurred in both, while reaction (d), giving $CH_4 + CO$ occurred in both.

Reaction (a) was the chief one in the experiment of Jackson and Northall-Laurie and probably the principal one for de Hemptinne, although in the latter's experiment reaction (d) also occurred because of the longer duration of the discharge.

Ethyl Alcohol

Ethyl alcohol has been subjected to photochemical decomposition in the same apparatus used for methyl alcohol by most of the investigators who worked with methyl alcohol. The following table is a summary of the results:

analogous to the action of some reagents, while reaction (2) is not effected by any chemical reagent. In the second place, methane is very stable and it is unlikely that it reacts with oxygen, in the electric discharge, to form carbon monoxide in more than traces. And thirdly, if methane could be as easily decomposed in the discharge as de Hemptinne would lead us to believe, it is very unlikely that it would ever be formed. It seems as if de Hemptinne reasons too much in a circle.

A more plausible explanation would be to assume that one primary action in the discharge is the splitting off of the hydroxyl group:

$$CH_3OH = CH_3 + OH$$
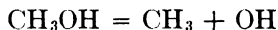
two of which combine to form water and free oxygen:

$$_2OH = H_2O + O$$

The CH_3 group then might react with hydrogen which has just been set free and form methane:

$$CH_3OH = _2H + HCHO$$
$$CH_3 + H = CH_4$$
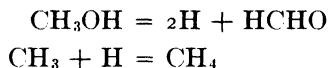
while the oxygen combines with the formaldehyde, giving water and carbon monoxide:

$$O + HCHO = CO + H_2O$$
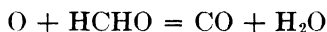
We would assume that there are three primary reactions:

$$CH_3OH = CO + _2H_2 \qquad (a)$$
$$CH_3OH = _2H + HCHO \qquad (b)$$
$$CH_3OH = CH_3 + OH \qquad (c)$$

and if (b) and (a) are combined in the manner just described, we have

$$CH_3OH = _2H + HCHO$$
$$\underline{_2CH_3OH = _2CH_3 + _2OH}$$
$$_3CH_3OH = _2CH_4 + _2H_2O + CO \qquad (d)$$
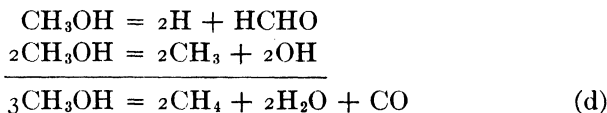
The results of Maquenne, Poma and Nesti, and de Hemptinne can be explained quantitatively on the basis of equations (a), (b), and (d). It will be noted that Maquenne obtains at each pressure approximately half as much CO as CH_4. Equation (d) gives this relation also. This equation plus (b) is a quantitative representation of Maquenne's results.

Maquenne expected his results at low pressures to be more exclusively those due to the primary reaction, and not to secondary reactions. While in some cases this may be true, it cannot be wholly true with methyl alcohol where there are probably three primary actions. There enters not only the question of primary reactions but also the concentration, in the vapor phase, of the products of the reaction. Acetylene is probably formed because of dehydration of the alcohol.

methane certainly yields water, one should not wonder about the presence of CO_2. Since the action of electric oscillations is a very complicated process, it is very difficult to explain the facts correctly, and any contingent assertions can be advanced only with much reserve. Meanwhile, I believe that one has a good basis for the assumption that, in the decomposition of methyl alcohol, the molecule first breaks down into oxygen and methane: $CH_3OH = CH_4+O$; other explanations are not permissible. The two usual ones are as follows:

"1. One can assume a decomposition into carbon monoxide and hydrogen, which is, however, very unlikely, since the analysis shows a large amount of methane, the presence of which is difficult to explain. The equation would read: $CH_3OH = CO + 2H_2$, and the methane would have to be formed from its elements. This is improbable, for according to the experiments of Berthelot a mixture of carbon monoxide and hydrogen, under the influence of electric oscillations, gives, besides carbon dioxide, a solid substance with the approximate composition $C_4H_5O_3 : 5CO + 3H = CO_2 + C_4H_5O_3$. The gas contains, also, traces of acetylene and unsaturated hydrocarbons, while in our experiments about 35% of methane is formed.

"2. One could assume that the hydroxyl is split off from the molecule and since it is only slightly stable, decomposes into oxygen and hydrogen, which in their turn react with the CH_3 group and give carbon monoxide, water, and methane. This hypothesis is slightly probable. In this case there must be as much carbon monoxide as methane, which is not the case. Moreover, how could the formation of so large an amount of methane be explained when this gas itself is decomposed by electric oscillations? One could still assume the formation of polymerized hydrocarbons from CH_3, but this assumption again does not explain the presence of methane and the other end-products."

Poma and Nesti also agree with a primary decomposition of the molecule into CH_4 and O as an explanation for the presence of methane. They assume three primary reactions as follows:

$$(1) \quad CH_3OH = CO + 2H_2$$
$$(2) \quad 2CH_3OH = 2CH_4 + O_2$$
$$(3 \quad CH_3OH = HCHO + H_2$$

The first undoubtedly occurs under the proper conditions. Jackson and Northall-Laurie offer some results which show that reaction (1) occurs under their conditions, almost to the exclusion of any other.

Poma and Nesti have shown that reaction (3) occurs, and Maquenne's results point in the same direction, since he undoubtedly had polymerized formaldehyde in the residue.

Neither of these reactions, however, explains the presence of methane, for which Poma and Nesti, and de Hemptinne offer equation (2). That this is a primary reaction seems unlikely. The formation of methane and the splitting off of oxygen with the subsequent decomposition of the methane to form other hydrocarbons and the reaction of the methane and oxygen to form carbon monoxide, water, and carbon dioxide is improbable for several reasons. In the first place, the action of the discharge as shown by reactions (1) and (3) is quite

"In short, in order to explain the formation of the gas which we obtain, the following equations may be assumed:

$$(1) \quad CH_3OH = CO + 2H_2$$
$$(2) \quad 2CH_3OH = 2CH_4 + O_2$$
$$(3) \quad CH_3OH = HCHO + H_2$$
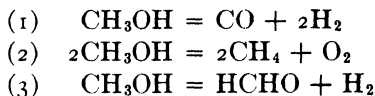
"The presence in our system of methane and the absence of oxygen and carbon dioxide indicate that the oxygen probably combines with the hydrogen to form water. Since our analysis showed two volumes of carbon monoxide to three volumes of methane, equations (1) and (2) may be combined to give equation (4):

$$(4) \quad 5CH_3OH = 2CO + 3CH_4 + 3H_2O + H_2.$$
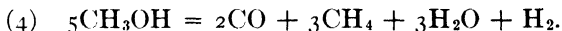
"As it appears from this equation that the volume of hydrogen given off in accordance with equations (1) and (2) should be equal to one-half the volume of carbon monoxide, it follows that in our experiments, the hydrogen should have been 5%. Consequently the hydrogen liberated exclusively in accordance with equation (3) should be approximately 68% of the total volume of gas and indicated that about two-thirds of the alcohol vapor loses hydrogen to form formaldehyde or its polymers.

"We combined the liquid from three flasks—from three ozonizers—this being the residue from about fifty hours' action. This was a clear alcoholic liquid, colored slightly yellow and having a strong formaldehyde odor, and giving a copious precipitate with bisulphite, indicating the presence of free formaldehyde in the alcoholic liquor.

"Most of the alcohol was distilled off on the water bath, leaving an oily yellow liquid of high density. A second distillation was made over a Wood's metal bath; the liquid distilled at 100° to 109° but most of it decomposed, giving off suffocating vapors of formaldehyde. A small residue was left of a liquid which rapidly turned brown and resinified without distilling.

"A part of the distillate congealed to a white crystalline mass which when redistilled, decomposed mostly to formaldehyde."

de Hemptinne[1] is quite positive that the primary reaction in the decomposition of methyl alcohol is: $CH_3OH = CH_4 + O$, but his explanation does not seem sound. "The molecule is decomposed into oxygen and methane, $CH_3OH = CH_4 + O$, and the oxygen reacts in turn on methane and forms carbon dioxide, carbon monoxide, and water, while at the same time methane itself decomposes into hydrogen and other hydrocarbons. The presence of carbon dioxide is surprising at first glance because there is an excess of methane over oxygen; one can, however, easily explain the appearance of CO_2. Maquenne[2] has shown that a mixture of carbon monoxide and water vapor gives carbon dioxide under the influence of electric oscillations. I can myself confirm this fact: a mixture of CO at 20 mm. pressure and H_2O at 6 mm. pressure gives after ten minutes 4% of CO_2. Since the action of oxygen on

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[1] Z. physik. Chem., **25**, 286 (1898).
[2] Compt. rend., **96**, 65 (1883.)

Of their results Berthelot and Gaudechon[1] say that "the photolysis of the primary functional alcohol group, CH_2OH is marked by the predominance of hydrogen, associated with carbon monoxide, and by the absence of carbon dioxide. Furthermore, in the first members of the fatty acid alcohols, of the type RCH_2OH, one finds in the gaseous state the hydrocarbons R_2 coming from the doubling of the radical R from two contiguous molecules.

"The essential feature[2] of the photolysis of alcohols is an abundant evolution of hydrogen (70% approximately of the total gas) with the formation of the corresponding aldehyde: $CH_3CH_2OH = H_2 + CH_3COH$. . . .

"We have verified likewise the formation of methyl aldehyde in methyl alcohol exposed to the rays. . . . The alcohol group,[3] CH_2OH, is split up, H_2 forming 60 to 70 volumes; and the residues, OH and C, react to give H_2O and the gas CO, which forms 10 to 20 volumes. The gas CO_2 appears only accidentally in the case of methyl alcohol, without doubt as a result of the secondary formation of a little formic acid, which decomposes in its turn. (The action of oxygen upon alcohol gives a notable quantity of formic acid, as we have ascertained directly)."

In other words, the primary reaction, according to them, is:

$$HCH_2OH = H + CH_2OH$$

which is followed by:

$$2H = H_2$$

and

$$2OH + C = H_2O + CO.$$
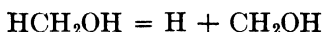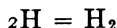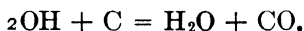
It is a little difficult to see just how they make these quantities balance.

The same considerations evidently cannot apply to the results of Maquenne,[4] who does not speculate on details. "The composition of the gas varies with the interior pressure because of the secondary reactions which take place between the products of the initial decomposition. These secondary reactions give birth to resinous bodies, less volatile, which consequently escape the analysis, and which one finds, at the end of the experiment, dissolved in the excess of methyl alcohol. These polymerizations take place with the liberation of hydrogen, as one observes ordinarily in pyrogenic reactions."

Maquenne here hints at a reaction which Poma and Nesti[5] discuss in some detail. It will be worth while to find out what they say before Maquenne's results are discussed.

"In order to free the gas from the alcohol and formaldehyde which were inevitably present, the first portions were washed in salt water. . . . The result of our experiments is interesting in view of the large proportion of hydrogen compared to methane and even more so because of the high ratio to carbon monoxide, indicating that in all probability under the conditions of our experiment, methyl alcohol is dehydrogenated to form a large proportion of formaldehyde or perhaps one or more of the polymers.

[1] Compt. rend., **151**, 1349 (1910).
[2] Compt. rend., **153**, 383 (1911).
[3] Compt. rend., **151**, 480 (1910).
[4] Bull., **40**, 61 (1883).
[5] Gazz., **51** II, 84 (1921).

Losanitsch and Jovitschitsch[1] used a "Berthelot" apparatus, while Losanitsch[2] alone, ten years later, used practically the same ozonizer.

"I have used[3] here the same Berthelot ozonizer which I used in my first experiments. On this apparatus I have provided only two changes, namely: on the inlet tube I placed a stopcock, with which I could hermetically seal the gas in the apparatus; and I have bent the exit tube down so that when it is immersed in mercury I can measure the pressure of the gases in the apparatus with it. In this way I have been able to appraise the velocity of the reaction so far as it is connected with condensation."

Losanitsch also mentions means of running experiments at higher temperature, and by using steam, goes to 100° or slightly higher. "When I wished to conduct this reaction at a higher temperature, I filled the apparatus with warm conducting acid. Or if a more intense heat was necessary, I covered the cylinder in which the ozonizer rested, with rubber tubing and through this led in steam."

Löb[4] used an ozonizer similar to that of Poma and Nesti to study the effect of the silent discharge on organic liquids. He, however, allowed the condensed vapor to flow back through the reaction chamber, whereas Poma and Nesti led them back into the vaporizing flask by means of a side tube. Löb studied the effect of both alternating and direct current. He gives[5] a detailed description of his apparatus, in order that no essential factor be neglected.

The essential features of the apparatus of several investigators have been described. We shall now review their results on methyl alcohol, ethyl alcohol, acetic aldehyde, acetic acid, and acetone, and attempt to classify and coordinate them, and harmonize them with the conditions of the experiment.

Methyl Alcohol

A summary of the results which have been obtained with methyl alcohol shows only slight concordance at first glance:

	CO	CO_2	CH_4	H_2	C_2H_2	C_2H_4
Berthelot and Gaudechon[6]	8.0	5.0	—	87.0	—	—
Maquenne[7] (3–4 mm.)	24.3	0.0	51.0	20.4	4.3	
(50 mm.)	21.8	0.9	43.2	33.7	0.9	
(100 mm.)	19.6	0.0	36.7	42.8	0.9	
Poma and Nesti[8]	10.8	—	15.5	73.3	—	—
de Hemptinne[9] (weak oscillations)	30.4	4.2	32.9	30.5	—	—
(strong oscillations)	28.0	3.0	35.0	32.0	—	—
Jackson and Northall-Laurie[10]	35.5	—	2.4	61.1	1.2	0.6

[1] Ber., 30, 135 (1897).
[2] Ber., 40, 4656 (1907); 41, 2683 (1908); 42, 4394 (1909).
[3] Ber., 40, 4656 (1907).
[4] Z. Elektrochemie, 12, 282 (1906).
[5] Loc. cit. p. 285.
[6] Compt. rend., 151, 479 (1910).
[7] Bull., 40, 60 (1883).
[8] Gazz., 51 II, 84 (1921).
[9] Z. physik. Chem., 25, 285 (1898).
[10] Loc. cit.

can be perceived by turning the head rapidly; these correspond to the interruptions of the Ruhmkorff coil."

Poma and Nesti increased the yield by connecting several ozonizers in parallel as shown in a sketch of their apparatus.[1] The nature of the discharge is similar to the ordinary silent discharge. They used a high-voltage alternating current, whereas most people use usually the oscillating current obtained from a Ruhmkorff coil. "We used[2] a small converter which . . . gave an alternating current of 46 cycles and 96 volts. This was raised to a maximum of about 10,000 volts by a small oil-cooled transformer. The conversion ratio was varied from 1 to 100, 1 to 75, and 1 to 50.

"The ozonizers of two coaxial glass tubes had an internal armature consisting of a light silver mirror deposit, formed by one of the usual reduction methods. The external armature consisted of a fixed net of fine iron wire.

"As shown in the diagram, the organic substance was placed in a glass flask and heated in a water bath or an oil bath. Reflux condensers on top of the ozonizers were connected with the flasks by side arm tubes so that the condensed vapors did not flow back through the apparatus.

"In order to have sufficient quantities of the reaction products for experimental studies, we made the apparatus in batteries of three or six units as shown in the diagram, electrically connected together. The condensers were connected with a gas sampling bulb so the uncondensed vapors could be withdrawn for analysis."

de Hemptinne was the first to use, so far as we know, anything approaching a high-frequency discharge when he used Lecher's apparatus[3] as a source of current. By using this apparatus he was enabled to secure a wide variation in wave-lengths.

"The vapors[4] of a series of substances were subjected to the influence of electric oscillators and the decomposition products analyzed according to the usual methods. The apparatus, in which the decomposition was accomplished, consisted of a wide glass tube about 75 cm. long and 4 cm. in diameter; at one end was the three-way stopcock R, at the other a graduated tube B, 75 cm. long, which is connected by means of a long rubber tube with the mercury reservoir C." Through the three-way stopcock, the decomposition tube could be pumped out and then "the gas being studied can be led in until the desired pressure is reached, e.g., 10 mm. On the two opposite sides of the decomposition tube is pasted tin foil which is connected with the wires of the Lecher apparatus. The interior of the tube may in this way be subjected to oscillations of the desired wave-length."

"The course of the reaction can be followed by observing the position of the mercury" in the tube connecting the mercury reservoir and the decomposition tube. When the decomposition is finished the apparatus is connected with a Hempel burette and the gas is drawn over for analysis.

[1] Gazz., **51** II, 89 (1921).

[2] Loc. cit. p. 83.

[3] Wied. Ann., **41**, 850 (1890).

[4] Z. physik. Chem., **25**, 284 (1898).

cm. wide, connected to earth. The action of the tin foil caused the discharge from the electrode" (in the middle of the bulb) "to spread all around and completely fill the bulb with a glow."

"The purified and dried liquid required was contained" in a bulb connected to the manometer side of the apparatus.

The idea which Jackson and Northall-Laurie expressed of being able to determine the initial reaction has been mentioned by others. Maquenne, who used a silent discharge on various vapours, had the same end in view.[1]

"One can observe that the decompositions effected by the silent electric discharge are ordinarily similar to those which heat produces. The analogy is evident for most of the gaseous binary compounds; I have tried to extend it to the more complex compounds by studying the decomposition of the first members of the fatty acid series in the discharge apparatus of Berthelot. One knows that, in that case, electricity, as well as heat, tends to produce secondary reactions which each time mask, by their importance, the initial reaction. I have succeeded in partially overcoming that difficulty by effecting the decomposition in a vacuum, maintained constant by an outflow of mercury; one thus removes the gases evolved by the action away from the discharge almost as soon as they are freed and before they have had time to react together. This method permits in addition the production of a vigorous discharge free from sparks, and the discovery of some of the most important secondary reactions, by studying the variations in composition of the gas obtained under a high or low vacuum.

"The apparatus employed was composed of a discharge tube according to M. Berthelot connected by a three-way stopcock to a mercury manometer and to the pump. The liquid to be studied is introduced at the bottom of the discharge tube and its vaporization is effected rapidly enough, for the moderately volatile substances, so that one obtains, at the pump, about 40 to 50 cc. of gas per hour. The decomposition is more rapid as the internal pressure is lower."

It seems as if what the pressure really measures must be the velocity of flow of the vapor through the apparatus. For different substances the pressure will have no relation unless it happens that the vapor pressure at the temperature of operation, and the rate of decomposition are the same. "The silent discharge tube of Berthelot" which Maquenne used was illustrated and described by Berthelot several years before.[2]

Dilute acid was used in the concentric tubes surrounding the reaction tube, as in the ordinary ozonizer and the discharge was furnished by[3] "a Ruhmkorff coil, the largest possible, operated with five or six large Bunsen cells. If more are used, the tube may be pierced; that inevitably happens when more than eight are used. . . .

"The discharge which is produced is silent and invisible in broad daylight; but at night, the tube or, more correctly, the annular space which contains the gas, appears illuminated by a phosphorescent glow, in which the alternations

[1] Bull., **39**, 306 (1883).

[2] Ann. Chim. Phys., (5) **10**, 75; **12**, 463 (1877).

[3] Loc. cit., **10**, 81.

In a subsequent paper of the series[1] the authors continue the description of the use of their apparatus. "In the study of organic compounds we have preferred the small lamp of 110 volts, of which the action is more manageable; in most cases the temperature was allowed to mount to 80° or 90°; in certain cases it did not exceed 50° or 60°. In general the evolution of gas stopped in-increasing at the end of about ten hours, and the state of equilibrium appeared established, for sensibly the same proportion of gas was found in many successive experiments."

Jackson and Northall-Laurie[2] used the high-frequency discharge, with several well-defined objects in mind. "Many experiments have been made on the behavior of various gases and vapors under the influence of electrical discharges, but so far as we know no experiments have been published dealing directly with the first change and not with the accumulated changes which occur when such vapours as those of methyl alcohol and acetaldehyde are subjected to the rapid oscillations of a high frequency discharge. . . .

"Qualitative experiments on the action of electric discharges on various saturated and unsaturated compounds led one of us to the conclusion that as a general rule the former were broken down to simpler molecules, whilst the latter were converted into complex polymerized substances.

"In the case of methyl alcohol and acetaldehyde, it was thought worth while to study the reaction quantitatively and to use the high-frequency current for the source of oscillation, as it would be possible in this way to avoid the effect of heat to the greatest extent.

"Moreover, by employing this form of current, relatively large volumes of the vapours could be used and the immediate, not the accumulated, effect on them could be studied."

Their apparatus "is a high-frequency machine similar to those used for therapeutical purposes, and consists of two Leyden jars with spark gap, the length of which can be adjusted, and a large solenoid on a drum which can be revolved and the length of wire in use adjusted by the position of the side terminal. This enables the apparatus to be 'tuned' to give the best results with the current and size of bulb used. One jar is connected to earth, and the two jars are connected on the inside with the secondary poles of a large induction coil capable of giving a spark of 50 cm. in length in air, and on the outside with each end of the solenoid. A current of 2 amperes at 100 volts was used in the primary coil."

The "bulb in which the decomposition took place" was round, and "about 12 cm. in diameter, with two side tubes joined" respectively to a vacuum pump and a manometer. "The platinum electrode . . . was made about 6 cm. long and 1.5 cm. in diameter, shaped like a small nutmeg grater. The pierced and roughened surface assisted in spreading the discharge." It was hung in the middle of the decomposition bulb. The bulb itself was hung inside a "large beaker, round the outside of which was fixed a strip of tin foil 7

[1] Compt. rend., 151, 479 (1910).
[2] J. Chem. Soc., 89, 1190 (1906).

experiments showed that it is high. A comparison with some of the results obtained by other workers will show its advantage in this respect.

Berthelot and Gaudechon[1] used a quartz mercury lamp. The organic liquid undergoing decomposition was contained in a quartz vessel which was held in close proximity to the lamp. The decomposition products, under these conditions, amounted to a few cubic centimeters per hour at the most. With some substances it was a fraction of a cubic centimeter per hour. Maquenne,[2] who used a silent discharge, obtained forty to fifty cubic centimeters of gas per hour. Jackson and Northall-Laurie[3] evidently obtained larger amounts of gas in the same length of time than any of the other investigators, although the exact amount is not stated. They used a high-frequency discharge.

With our apparatus we were able to obtain from ten to several hundred cubic centimeters of gas per minute. This made the analysis easier and more accurate. More important still, if one of the products happened to be present in a small percentage, it was detected more readily.

Literature

The compounds which were studied in this work were acetone, methyl alcohol, acetic acid, ethyl alcohol, acetic aldehyde, a mixture of sulfur dioxide and oxygen, and a mixture of ethylene and acetylene. The literature shows that a considerable amount of investigation had already been made on these substances. To some of this work reference has already been made and it has been stated that the investigators who have been mentioned above used different sources of radiant energy. In general there are three classes: the quartz mercury lamp, the silent electric discharge, and the high-frequency electric discharge. It has not been possible in every case to find out in detail what kind of apparatus was used in the experimental work but the references given below provide information sufficient for our purpose.

Berthelot and Gaudechon were the only investigators, of those to be mentioned, who used a quartz mercury arc. In their description[4] they say:

"The chemical action of ultra-violet rays, recognized for a long time in photography, can be now produced with great intensity by means of a quartz mercury vapor lamp.

"We have employed either an Heraeus lamp of 110 volts consuming 2.5 amperes in normal operation and of which the arc is 4 cm. long, or a Westinghouse lamp of 220 volts, consuming 5 to 6 amperes and with an arc 5 to 6 cm. long. The carefully dried gases, subjected to the rays, were enclosed in a quartz tube about 0.6 mm. thick. The pressure was in the neighborhood of 75 cm. Under these conditions, the gases were ionized and became conductors, and remarkable chemical effects were produced."

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[1] Compt. rend., **150**, 1169 (1910).
[2] Bull., **39**, 307 (1883).
[3] J. Chem. Soc., **89**, 1192 (1906).
[4] Compt. rend., **150**, 1169 (1910).

shall, at least for the present, treat the reactions which take place in the Tesla discharge as purely photochemical.

It is, of course, true that the spectrum for every gas is characteristic. That this is true limits very definitely the reactions which can take place. No primary photochemical reaction can be made to occur if the necessary wave-length is absent. Conversely, any photochemical reaction tends to occur if the proper wave-length is present. The photochemical reactions which tend to take place are therefore limited first of all by the radiation which is produced by the passage of the discharge through the gas. Whether the reactions actually do take place and the extent to which they occur depends on the energy relations. Considering a specific case, it might be true that the passage of the Tesla discharge through ethyl alcohol produces only the wave-length which is necessary to dehydrogenate the alcohol and does not produce the necessary radiation for dehydration. Hence, hydrogen and acetaldehyde would be formed, but no ethylene and water. It is more likely, of course, that both wave-lengths or

FIG. 2

bands are produced. As a matter of fact, both reactions do occur in ethyl alcohol, although the dehydrogenation occurs to the greater extent, probably because it requires less energy.

To be so limited in possible reactions by the almost accidental presence of the proper radiation, or in the extent to which a given reaction can occur by the almost fortuitous quantity of energy produced is a condition which could with advantage be changed. One possibility lies in the variation of pressure or voltage, or frequency. There is another possibility which is very attractive. It is based on the work of Cario and Franck.[1] When hydrogen is illuminated by a quartz mercury lamp there is no evidence of the formation of hydrogen atoms. But Cario and Franck showed that if mercury vapor is introduced into the hydrogen, it gives out radiation, under the influence of the ultra-violet light, which is capable of forming and does form hydrogen atoms from the molecules of hydrogen which are present.

If this principle is of general application, then there is a wide field for using it in connection with the Tesla discharge. Unfortunately, we have not yet been able to obtain any positive results. But there is still reason to believe that by the use of the proper substance in the discharge tube, a desired reaction could be made to occur. In the case of ethyl alcohol, which has already been cited, excitation of the alcohol molecule by the proper second substance, which in turn is influenced by the discharge itself, might result in a high yield of ethylene instead of a high yield of hydrogen, as at present.

That the Tesla discharge proved to be a convenient source of photochemical energy for our high-temperature ozonizer was the chief reason for using it. We hoped, however, that the rate of decomposition would be high, and our

[1] Z. Physik, 12, 162 (1922).

and Löb used as sources of radiant energy a quartz mercury lamp, an ordinary ozonizer, or a high-frequency discharge. With these sources they effected the decomposition of some of the organic compounds with which we proposed to work and their results with different sources on the same compound showed that in so far as the nature or amounts of the products is concerned, the energy sources are more or less comparable.

The following results are typical as an example from which this conclusion is reached. These figures give the percentage of decomposition products from methyl alcohol:

	CO	CO$_2$	H$_2$	CH$_4$	C$_2$H$_2$ or C$_2$H$_4$
Berthelot and Gaudechon[1]					
(quartz mercury lamp)	8.0	5.0	87.0	—	—
Maquenne[2]					
(silent discharge)	19.6	—	42.9	36.7	—
de Hemptinne[3]					
(silent discharge)	30.4	4.2	30.5	32.9	small
Jackson and Northall-Laurie[4] (high frequency discharge)	35.5	—	61.1	2.4	1.8

The products are in general the same. The percentages are different in some cases, which may show that a different point of equilibrium is attained, or that some decomposition of the initial product occurs.

It is evident that if photochemical decomposition occurs when an electric discharge is passed through a gas or vapor, then the radiation which causes this reaction must be formed in the gas itself. We would therefore expect some relation between the emission and absorption bands of a gas. The question then is this: will the radiation which is formed in the vapor be absorbed by the vapor? In order to determine that point a Tesla discharge was passed through bromine vapor and the spectrum photographed (Fig. 2a). Then a spectrophotograph was made of the discharge in air (Fig. 2b). Next, between the spectrograph and the discharge tube (with air) was placed a 3 mm. layer of bromine vapor; the spectrophotograph thus made is shown in Fig. 2c. It is observed that the bromine vapor has absorbed those bands in the air spectrum in the same general region where it itself emits radiation in the Tesla discharge.

This does not prove that the absorbed radiation causes any photochemical action; it shows only that a substance can absorb light in the same general region in which it itself emits light in the Tesla discharge. This absorbed light will tend to decompose the vapor which absorbs it and for that reason we

[1] Compt. rend., **151**, 479 (1910).
[2] Bull., **40**, 60 (1883).
[3] Z. physik. Chem., **25**, 285 (1898).
[4] J. Chem. Soc., **89**, 1192 (1906).

energy, but to use the ordinary type of ozonizer containing sulfuric acid or any other conducting liquid at a high temperature would be entirely out of the range of practical possibility. The danger of breakage and the difficulty of making the necessary gas and electrical connections made it appear unprofitable to spend any time on the ordinary type of apparatus. We devised, therefore, an entirely new ozonizer for the specific purpose which we wanted it to serve. It consisted essentially of two concentric glass tubes, of suitable size and length. The center portion only of these tubes was made conducting by means of a metallic coating on the outside of the outer tube and the inside of the inner tube. The gases or vapors in which the reaction was taking place passed through the space between the tubes.

Because the metallic coatings in the center extended for only one-third of the total length of the tubes, and the Tesla discharge passed between these coatings, it was necessary to heat only this portion, together with a short length on either end of the coating. Thus the ends of the tubes remained cool and enabled the proper connections to be made with the greatest ease. A more detailed description of the apparatus will be given later.
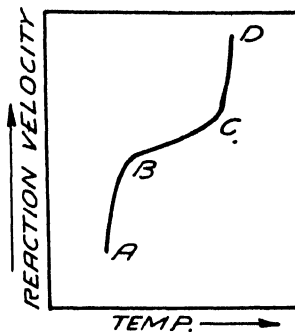
Fig. 1

In addition to investigating depolarization by heat, it seemed to us that certain organic compounds offered an attractive field for photochemical work because of the possibility of carrying out reactions similar to those obtained by the use of catalysts. Alcohol can be decomposed in two ways catalytically. If alumina is used, alcohol is dehydrated, forming ethylene and water, while with nickel as a catalyst dehydrogenation occurs, with the formation of hydrogen and acetaldehyde. To duplicate these reactions photochemically seemed an attractive possibility and our second object in this work was to discover, so far as possible, the course of the photochemical reactions in the decomposition of certain organic compounds.

Grotthuss, in 1818, formulated the law that only that light which is absorbed by a substance can cause chemical change. In 1912 Bancroft proposed the following improved generalization: "All radiations which are absorbed by a substance tend to eliminate that substance. It is entirely a question of chemistry whether any reaction takes place or what the reaction products are." We may go further and say that any particular reaction tends to take place photochemically if the right wave-length is absorbed. But the wave-length which will be absorbed and cause a particular reaction must be provided and in photochemical work its presence becomes our first concern. In our work we elected to use the Tesla discharge as a convenient source of radiant energy. The question immediately arose whether its action is strictly comparable to that of a source of pure photochemical energy such as the quartz mercury lamp. Several separate pieces of evidence seemed to show that it is. Berthelot and Gaudechon, Maquenne, de Hemptinne, Jackson and Northall-Laurie,

the temperature coefficient should be smaller. But there is some reason to believe that it may also become larger at lower temperatures. Chlorine and hydrogen unite explosively in sunlight at ordinary temperatures but Amato[1] reports that at $-12°$ the reaction does not occur even when the mixture is kept in bright sunlight for several hours. The temperature coefficient of this reaction is given as 1.0–1.04,[2] but it is evident that if Amato's result is correct, the coefficient must be much higher than this in the temperature range from $-12°$ to about $+15°$.

Dewar conducted some interesting experiments on photographic paper and plates. He found that paper[3] becomes insensitive to ordinary light when held at liquid air temperatures but the photographic action of ultra-voilet light is not entirely prevented. This might mean that the temperature coefficient is different for different wave-lengths but the result is probably more related to the greater sensitivity to ultra-violet light. In 1896 Dewar reported at the Royal Institution that at a temperature of $-180°$ certain sensitive films were reduced in sensitiveness to less than a quarter of that which they possess at ordinary temperatures. If the so-called temperature coefficient were uniform over this entire range (from $20°$ to $-180°$) it would have a value of about 1.07. He found also in experiments with liquid hydrogen, at $-252°$, that the loss in sensitiveness becomes asymptotic as absolute zero is approached, which points to a different coefficient in the extreme lower range.

From Abney's work[4] it appears that the coefficient for a certain photographic plate may be higher than that found by Dewar. In 1893 Abney found that a plate often required double the exposure when the temperature decreased from $33°$ to $-12°$, a drop of about $40°$. This corresponds to a so-called temperature coefficient of approximately 1.19 as compared with Dewar's result of 1.07.

The general conclusion at which we must arrive is that the temperature coefficient does vary in different regions of temperature, and the general curve showing the relation between temperature coefficient, sensitivity or reaction velocity and temperature must be like this:

In the specific case of hydrogen and chlorine, for example, the portion of the curve BC must be very short if Amato's results are correct.

In the case of acetaldehyde our work has confirmed the portion BCD. Acetaldehyde begins to decompose thermally at about $400°$. If at temperatures approaching this thermal decomposition point, the molecule becomes more instable, light should have less work to do in decomposing the molecule of acetaldehyde and we should expect an increase in the rate of decomposition and in the so-called temperature coefficient. In order to investigate this question it was first necessary to devise an apparatus in which photochemical reactions could be brought about at temperatures up to $350°–400°$. It seemed to us that an ozonizer would be a convenient source of photochemical

[1] Amato: Gazz., **14**, 57 (1884).

[2] Taylor: 1242.

[3] Collected Papers: **2**, 1030.

[4] Proc. Royal Soc., **1893**.

EXPERIMENTS WITH A HIGH-TEMPERATURE OZONIZER

BY RAYMOND P. ALLEN

Introduction

It has been stated by Bancroft[1] that "the chemical effect of light is merely to eliminate, if possible, the substance absorbing the light. Whether that elimination takes place as a result of oxidation or of reduction is a matter which is quite independent of the light and which depends on the nature of the depolarizer. . . . We distinguish between chemical depolarizers or sensitizers and optical ones. The action of the chemical depolarizers is quite simple. If we take a ferric chloride solution and expose it to light, we might hope to get ferrous chloride and chlorine; but the two could not co-exist and therefore would be formed only to a slight extent, if at all. If we take an alcoholic solution of ferric chloride, the chlorine can react with the alcohol. It therefore takes less energy to reduce or decompose ferric chloride in alcoholic solution." Actually, there is a photochemical change under these conditions.

This principle can be extended in a general way to include other depolarizers which are not ordinarily considered as such. We are particularly concerned here with the effect of the photo-sensitivity of a substance when the temperature of that substance is changed. If we have a substance which we wish to decompose by means of light, we may find that an ordinary source of energy decomposes the compound very slowly, or not at all. If the temperature is raised, however, it should be possible for the same radiant energy to cause the reaction to occur more rapidly because the compound has been raised to a temperature closer to its thermal decomposition point; the molecule has become more instable and consequently the light has less work to do. In this case the effect of raising the temperature is similar to the action of a depolarizer or sensitizer. This appears to contradict the idea which has been held that the temperature coefficient of photochemical reactions is almost unity.[2] By temperature coefficient of a reaction the physical chemist means something quite different from what his words should mean. He means the ratio of the velocities at ten-degree intervals. If a reaction velocity is independent of the temperature, the ratio of the velocities at ten-degree intervals is unity. The real temperature coefficient is zero. While the ratio of the reaction velocities for ten-degree differences may be almost unity over certain ranges of temperature, it must be true that at temperatures approaching the point of thermal decomposition, the so-called temperature coefficient of photochemical decomposition increases rapidly.

The converse of this principle should also be true. If a given system becomes more stable at lower temperatures, it should be less photo-sensitive and

[1] J. Phys. Chem., **32**, 531-2 (1928).

[2] Taylor: "Treatise on Physical Chemistry," **2**, 1241 (1924).

Poma and Nesti considered the reaction with ethyl alcohol to be similar to that with methyl alcohol but "as may be seen, the greater complexity of ethyl alcohol makes the reaction also more complex but still there is a predominance of hydrogen. . . . "In this case, also, the residue was clear and yellow and gave a copious precipitate with bisulphite, i.e., the bisulphite compound of acetaldehyde. The distillation residue was a complex mixture which decomposed and resinified in part, liberating acetaldehyde."

de Hemptinne used the same experimental conditions as with the methyl alcohol.

"The analysis shows the absence of those hydrocarbons which are absorbed by fuming sulfuric acid; the remaining hydrocarbons belonged, therefore, to the C_nH_{2n+2} group. . . . Through calculations one can easily find the quantity of ethane and be convinced that it is not unimportant. The exact knowledge of the quantity relations of ethane to methane is not considered important for theoretical considerations but the fact itself that a considerable quantity of ethane is formed, is important. (Here, as later, the hydrocarbon richest in carbon continually appears in considerable quantities. I did not especially make a note of this quantity because it is different according to the experimental conditions.)

"Methane is formed through a secondary reaction from ethane, just like a series of more solid and resinous decomposition products. If one does not consider these side reactions, considerations similar to those obtaining with methyl alcohol lead to the conclusion that the molecule of ethyl alcohol will split up according to the equation: $C_2H_5OH = C_2H_6 + O$. One can scarcely explain in any other way the large amounts of ethane which appear. The assumption that decomposition into $CO + CH_4 + H_2$ occurs is not valid because ethane cannot be formed from methane and carbon monoxide. In order to meet all objections which would be raised against this explanation, we wish to allow the electric oscillations to act on alcohol vapor in the presence of phosphorus. If free oxygen is formed, part of it would have to be absorbed and the quantity of carbon monoxide would have to become smaller.

"This experiment had to be made in one of the earlier, somewhat different apparatus. Since the relative amounts of decomposition products depended on the dimensions of the apparatus, I made two preliminary experiments without phosphorus:

CO_2	2 %	
C_nH_{2n}	0.5	II
CO	15	
H_2	20	
$C_2H_6+CH_4$	62.5	

"The second analysis gave essentially the same result as the first.

"The action of the electric oscillations on alcohol vapor at the pressure and under the same conditions as above but in the presence of phosphorus gave:

CO	7%
C_nH_{2n}	1
H_2	65
$C_2H_6+CH_4$	27

"The action took place in the same time and with the same intensity as above. One sees that the quantity of carbon monoxide is smaller and of free hydrogen much greater. This phenomenon is easily explained, if one assumes that oxygen set free from the molecule becomes bound to the phosphorus. The disappearance of the carbon monoxide is not complete because it is impossible to expose every part of the vapor of the reaction to the phosphorus; and since the latter can absorb only that immediately surrounding, a part of the oxygen molecules withdraw themselves from this action and react with C_2H_6.

"My conclusions are confirmed under the experiment to be described with acetone. It was shown that acetone decomposes according to the theory into C_2H_6 + CO and that the quantity of carbon monoxide does not decrease in the presence of phosphorus, so that no free oxygen is therefore formed.

"Suppose we assume that the alcohol molecule decomposes according to $2C_2H_5OH = 2C_2H_6 + O_2$; if we now mix oxygen and ethane in this proportion, subject the mixture to the influence of electric oscillations for the same length of time and under the same conditions as before, then we obtain:

carbon dioxide	6%
carbon monoxide	15
hydrogen	34
ethane and methane	45

"These proportions of quantities approach those of experiment II; the same quantity of carbon monoxide appears but more carbon dioxide, which is easy to explain on the ground that the gas mixture is really always richer in oxygen than when the molecule decomposes into $2C_2H_6$ + O_2, because in the latter case the oxygen is still surrounded by alcohol vapor which it can oxidize in turn.

"A question now involuntarily obtrudes itself: how is it possible that oxygen splits away from the C_2H_6 group, in order to react with it again later?

"One can answer to this question, that in the molecule C_2H_5OH the grouping of C_2H_6 is not the same as that of the molecule C_2H_6, consequently the oxygen can separate completely from the molecule C_2H_5OH, whereupon the hydrogen atoms assume a new equilibrium position relative to the carbon and form a new ethane nucleus which can be attacked by oxygen. In other words, nothing else is to be said than that molecular nuclei of the same composition but different atom grouping have different affinity to one and the same element and will be attacked by this element in different ways. This is a well-known phenomenon in chemistry and to give only one of the many examples, let us consider that normal butyl alcohol gives butyric acid

upon oxidation, while the secondary alcohol goes over to the methyl-ethyl ketone and the tertiary alcohol or trimethylcarbinol yields acetone, acetic acid, and carbon dioxide."

This explanation is ingenious but de Hemptinne entirely overlooked the presence of acetaldehyde in the decomposition of ethyl alcohol. The primary reaction probably being $C_2H_5OH = H_2 + CH_3CHO$, had the phosphorus then inhibited the decomposition of the acetaldehyde, the results would be just what he obtained, i.e., a larger relative amount of hydrogen and smaller amounts of the hydrocarbons and carbon monoxide but essentially the same ratio of hydrocarbon to carbon monoxide. The fact that this ratio is fairly close indicates that this explanation is reasonably possible:

	Without P	With P
$C_2H_6+CH_4/CO$	4.17	3.86

It would be interesting to know the relative rates of decomposition with and without phosphorus.

Löb[1] believed that Maquenne obtained methane and not ethane. "Methane is not specified; yet, it seems to me unquestionable, according to de Hemptinne's experiments and my own, that the saturated hydrocarbons consisted for the most part of methane, which Maquenne did not expect among the decomposition products and therefore overlooked. In any case the occurrence of the reaction $CH_3.CH_2OH = CH_3CHO + H_2$ is to be seen with certainty from his experiments, since otherwise the presence of aldehyde cannot be explained. Since aldehyde itself yields principally methane and carbon monoxide and the latter is copiously formed in the gas mixture, so must the former also be present in the gas mixture as experiment with pure acetaldehyde shows. If one considers this as a secondary synthetic product, however, which is very improbable, its components still remain methane and carbon monoxide."

Löb[2] described his purpose as follows: "The results heretofore obtained are not comparable with my results as they stand, since they were obtained under different experimental conditions. Maquenne and de Hemptinne worked with reduced pressures, Berthelot in the presence of nitrogen. From that it appeared important to me to obtain next a picture of the decomposition of alcohol under atmospheric pressure in the absence of other substances in order to find out the influence of water and some gases. In accordance with the discussion given in the theoretical part, it was necessary to investigate acetaldehyde and acetic acid also; the behavior of the other substances formed by the action of the discharge on alcohol has already been called to notice in the first part of this work.

"The decomposition of absolute alcohol was undertaken in the electrisator provided with an inner condenser and a ground-polished little flask which had already served for the formaldehyde and formic acid experiments.

[1] Z. Elektrochemie, 12, 302 (1906).
[2] Z. Elektrochemie, 12, 308 (1906).

"The results of several analyses of the gases are as follows:

TABLE I

No.	Current	Amp.	Gases obtained from Reaction in cc.				
			CO_2	CO	H_2	C_nH_{2n+2}	C_nH_{2n}
1	Alternating	6.5	0.2	1.6	27.8	7.9	3.2
2	"	8.6	0.2	—	11.9	4.0	1.4
3	Direct	2.5	0.6	3.4	42.5	13.8	2.0

TABLE II

No.	Composition in Volume Percentage				
	CO_2	CO	H_2	C_nH_{2n+2}	C_nH_{2n}
1	0.5	3.9	68.3	19.4	7.9
2	1.1	—	68.0	22.9	8.0
3	1.0	5.5	68.2	22.1	3.2

"With alternating operation about 50 cc. were formed in two hours, while with direct current about 70 cc. in one hour were developed. In every case copious amounts of acetaldehyde were formed, so that, as the gas analyses further proved, the principal decomposition to occur was according to the equation: $CH_3CH_2OH = CH_3CHO + H_2$. The hydrocarbons C_nH_{2n+2} consisted chiefly of methane and ethane; the hydrocarbons C_nH_{2n} were nearly exclusively ethylene. The splitting of acetaldehyde remained secondary. The small amounts of carbon monoxide were easily explained from the large excess of hydrogen, which reduced the carbon monoxide for the most part to hydrocarbons.

"For comparison with the chief experiments it was necessary to find out the behavior of alcohol vapor at ordinary temperatures also. A difficulty existed therein in that most gases react with alcohol or with its decomposition products under the influence of the discharge. I finally chose nitrogen, which according to Berthelot's statement is absorbed only slowly, and made the experiment in the manner described in the electrisator for moist gases, in which I used 50% alcohol as the filling liquid, which also was used for the other combinations. The discharge space was filled completely with nitrogen and several cubic centimeters of the dilute alcohol were placed in the spherical enlarged part of the electrisator. This and all of the following experiments were carried out in a closed electrisator.

"The results of a two-hour experiment made with direct current of 2.5 amp. are as follows:

CO_2—1.6; CO—2.0; H_2—17.2; hydrocarbons—5.1 cc. and in volume percentage:

CO_2	6.2
CO	7.7
H_2	66.4
hydrocarbons	19.7

"The reaction liquid contained, detected at once by odor, acetaldehyde.

"In this and the last experiment of Table I the presence of formaldehyde was established. The carbohydrate reaction failed to appear in every case.

"The decomposition picture is essentially the same at ordinary temperatures as at the boiling point of alcohol. Only the presence of water leads to the more copious appearance of carbon dioxide from carbon monoxide whose reduction becomes less at the lower temperatures. The hydrocarbon consisted predominantly of methane, so that both typical reactions stood out sharp."

It seems probable that there are two primary reactions in the photochemical decomposition of ethyl alcohol: one, the formation of hydrogen and acetaldehyde; the other the dehydration of the alcohol to give ethylene and water. The photochemical decomposition of the aldehyde then follows with the formation of carbon monoxide and methane. Because of this primary decomposition of alcohol into aldehyde, the photochemical reactions of these should be considered together. Before proceeding with any further discussion of the alcohol reactions, those of acetaldehyde will, therefore, first be described.

Acetic Aldehyde

The following table shows the results which have been obtained in the photochemical decomposition of acetic aldehyde:

	CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon	5.0	39.0	33.0	23.0*	
Losanitsch	—	high	low	high**	low
Löb (25% solution)	6.7	33.0	32.5	27.8**	
de Hemptinne		41.0	20.0	39.0**	
Jackson and Northall-Laurie		45.2	0.4	44.2**	8.6***

    *C_2H_6
    **CH_4
    ***C_2H_2

Berthelot and Gaudechon[1] conclude that the photochemical reaction with acetaldehyde is

$$2CH_3CHO = C_2H_6 + 2CO + H_2.$$

"The photolysis of the primary aldehyde group COH is characterized by the predominance of carbon monoxide. It is accompanied by hydrogen. One also finds a few cubic centimeters of carbon dioxide. That corresponds actually to the point of view of oxidation, the aldehyde stage being intermediate between the alcohol stage and the acid stage.

"In the evolved gaseous mixture, with the first members of the fatty acid series RCOH, we have detected the hydrocarbons R_2 formed by the doubling of the radical R; with the higher members of the normal chain series, the hydrocarbons R_2 are no longer formed, they not being gaseous."

Losanitsch[2] concluded that the principal reaction results in the formation of carbon monoxide and methane, but claimed to have found also hydrogen,

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[1] Compt. rend., 151, 1351 (1910).

[2] Ber., 42, 4397 (1909).

ethylene, and formaldehyde. "Acetaldehyde[1] condenses under the action of the silent electrical discharge with strong liberation of gas (up to 20 bubbles per minute), whereby about 80% of the aldehyde used is decomposed and only 20% condenses. This gas consists of equal volumes of carbon monoxide and methane, besides a small amount of hydrogen and ethylene. The principal decomposition of acetaldehyde is therefore:

$$CH_3CHO = CO + CH_4.$$
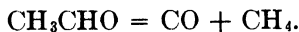
"Moreover, a considerable amount of formaldehyde is formed which further polymerizes.

"That portion of the acetaldehyde condensed by the discharge is a greenish yellow, mobile liquid which has an aldehyde odor and also shows aldehyde reactions. It is easily soluble in alcohol and ether, but only partially in water.

"The crude product boils from 70° to 190°; the distillate has a greenish yellow color and pungent odor. The fresh distillate does not act on litmus paper, but with standing the reaction becomes strongly acid, which in any case is to be attributed to oxidation of the aldehyde. By distillation I have obtained the following products:

B.P.	70-90°	100-120°	130-150°
C	45.31	45.51	49.02
H	9.75	8.62	8.12
O (diff.)	44.94	45.87	42.86

	Corresponding formula		
	$C_4H_{10}O_3$	$C_8H_{16}O_6$	$C_9H_{18}O_6$
C	45.28	45.71	48.65
H	9.44	8.58	8.11
O	45.28	45.71	43.24

"According to their composition these compounds are all aldehyde-like polymers of acet- and formaldehyde:

$$C_4H_{10}O_3 \text{ is } 2C_2H_4O.H_2O$$
$$C_8H_{16}O_6 \text{ is } 2CH_2O.3C_2H_4O.H_2O$$
$$C_9H_{18}O_6 \text{ is } 3CH_2O.3C_2H_4O$$
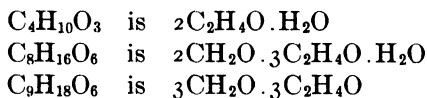
"The diacetaldehyde hydrate, $2C_2H_4O.H_2O$, is in any case the first anhydride of acetaldehyde hydrate."

$$CH_3.CH.O.CH.CH_3$$
$$\overset{\|}{OH} \quad \overset{\|}{OH}$$
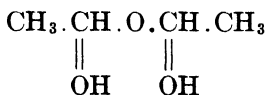
Löb's results cannot be compared directly with the others because he used an aqueous solution of aldehyde. "In the absence of water the vapor of acetaldehyde decomposed into methane and carbon monoxide; the methane yielded free hydrogen. In the presence of water a partial conversion of the carbon monoxide occurred into carbon dioxide and hydrogen, whereby the

content of the latter is increased. The results of an experiment of three hours' duration with a 25% aqueous solution under an atmosphere of nitrogen, with direct current, were as follows:

	cc	%
CO_2	1.4	6.7
CO	6.9	33.0
H_2	6.8	32.5
CH_4	5.8	27.8 "

de Hemptinne obtained these same gases in different proportions.

"Under the same conditions as with the other substances aldehyde gives:

carbon monoxide	41%
hydrogen	20%
methane	39%

"Aldehyde therefore decomposes according to this equation: $CH_3CHO = CO + CH_4$. It is interesting to compare aldehyde with acetic acid, which gives $C_2H_4O_2 = C_2H_4 + O_2$ and shows us how the mutual attraction of the elements can be changed through the introduction of an atom of oxygen in the molecule."

Jackson and Northall-Laurie found evidence of two distinct reactions.

"In the case of acetaldehyde a double reaction apparently takes place. Analyses of many samples of the gaseous products showed the presence of methane, carbon monoxide, and acetylene in large quantities, together with a very little hydrogen and other hydrocarbons. The proportions of these gases varied somewhat, but by working with discharges of very short duration it was possible to prove that the vapors of acetaldehyde decomposed partly into carbon monoxide and methane and partly into acetylene and water.

"The average composition of the gas freed from water and the vapor of aldehyde and obtained with discharges of short duration is shown by the following numbers:

CO	CH_4	C_2H_2	H_2
45.2	44.2	8.6	0.4

(percentage by volume)

"The presence of water as one of the products was ascertained in each experiment, but it was found difficult to obtain concordant results for the small amounts formed. From these numbers it will be seen that about eighty percent of the vapor of the aldehyde yielded carbon monoxide and methane, whilst the remainder was converted into acetylene and water. The changes took place apparently simultaneously and were the primary reactions, whilst the formation of any hydrogen and other hydrocarbons was probably due to secondary changes, as the amounts of the gases only became appreciable when the discharge was continued for a minute or two. A relatively considerable quantity of the main products was obtained by a mere flash of the discharge.

"The reaction giving rise to acetylene and water is apparently a reversible one, as when steam and acetylene were subjected to the discharge it was found possible by removing the products quickly to detect an aldehyde readily and to prove that it was acetaldehyde. An aldehyde was also obtained from carbon monoxide and methane treated similarly, but the quantity was small and there was certainly some formaldehyde produced. It is 'possible that the greater readiness of acetylene and water to form aldehyde may well account for the observed fact that the proportion of acetylene and water to carbon dioxide and methane was greater the shorter the duration of the discharge.

"We conclude, therefore, that the immediate action of high frequency discharges on the vapor of acetaldehyde is represented by the equations:

$$CH_3.CHO = CO + CH_4$$
$$CH_3.CHO = C_2H_2 + H_2O."$$
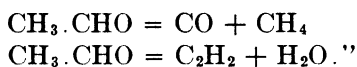
From the results so far reviewed, of the action of the electric discharge on ethyl alcohol, there is every reason to believe that the chief primary decomposition is into acetaldehyde and hydrogen. Occurring, also, but to a less extent, is the decomposition into ethylene and water. Every investigator, with the exception of de Hemptinne, detected the presence of large amounts of acetaldehyde. It is inconceivable that among his decomposition products, this compound was not also found, particularly since the analysis of his gaseous product shows substantially the same composition as that obtained by the others.

Furthermore, with regard to his results, it was shown (p. 1619) that in his experiments in the presence and absence of phosphorous, the ratio of carbon monoxide to hydrocarbon remained essentially the same, which would lead to the conclusion that the effect of the phosphorus is to retard the decomposition of the aldehyde which is first formed.

Because ethyl alcohol is decomposed first into acetaldehyde and hydrogen, it follows that any other gaseous products, with the exception of ethylene, probably come from subsequent decomposition of the acetaldehyde. The first photochemical action on the acetaldehyde is the splitting off of the CO group:

$$CH_3CHO = CH_3 + H + CO$$

which explains the relative abundance of this gas in the evolved products.

After this first separation there are two possibilities: either the formation of CH_4 from the CH_3 and H or the formation of C_2H_6 and H_2. Leaving out for the moment the decomposition into acetylene and water, acetaldehyde may therefore be decomposed photochemically in two ways:

$$2CH_3CHO = C_2H_6 + H_2 + 2CO \tag{1}$$

$$CH_3CHO = CH_4 + CO \tag{2}$$
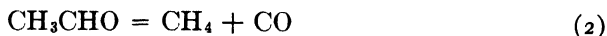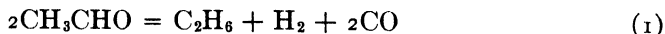
In whichever way the decomposition occurs, the amount of CO should be equal to the total amount of C_nH_{2n+2} and H_2. But only Jackson and Northall-

Laurie (and possibly Losanitsch) obtained this result, and it must be concluded that the CO first formed, disappeared by some subsequent reaction or dissolved in the condensed liquid.

If ethyl alcohol goes first to acetaldehyde and the latter then decomposes as just shown, it would be expected that the ratio of CO to C_nH_{2n+2} will be the same for alcohol and aldehyde in any given apparatus. Only two sets of results are available to test this hypothesis:

		Vol. CO	Vol. C_nH_{2n+2}	CO/C_nH_{2n+2}
Berthelot and Gaudechon	C_2H_5OH	22	15	1.5
	CH_3CHO	39	23	1.7
de Hemptinne	C_2H_5OH	22	48	0.46
	CH_3CHO	41	39	1.05

It must be concluded that some other reaction occurs in order to give such divergent results as those of de Hemptinne. Those of Berthelot and Gaudechon are close enough to lend some support to the hypothesis.

Acetone

A consideration of the results which have been obtained show that the photochemical decomposition of acetone is not a simple breakdown into CO and C_2H_6:

	CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon	—	49.0	—	51.0[*]	—
Maquenne low pressure	1.1	37.5	24.7	32.4[**]	4.3
" 50 mm.	1.1	40.0	25.7	29.7[**]	3.5
" 100 mm.	0.6	42.1	24.4	30.0[**]	2.9
de Hemptinne	2.0	48.5	11.0	37.0	1.5
Poma and Nesti	1.6	38.1	—	55.3	5.0[***]

[*]5% CH_4; 46% C_2H_6
[**]C_2H_6
[***]$C_2H_2 + C_2H_4$

Berthelot and Gaudechon find the photochemical decomposition of acetone very simple. "Ordinary acetone decomposes in a few minutes and gives 49 volumes of CO and 51 volumes of a mixture which is composed of 46 volumes of ethane and 5 volumes of methane. The aqueous solution of acetone gives 1 volume of CO_2, 44 volumes of CO, and 55 volumes of a mixture which comprises 46 volumes of C_2H_6 and 9 volumes of CH_4.

"The high proportion of carbon monoxide as well as the rapidity of evolution is a conspicuous characteristic of the ketone group and has already been pointed out for levulose. . . .

"In no case does the decomposition of a ketone give hydrogen. That distinguishes them from the aldehydes and corresponds entirely to the difference in the formulas CO and CHO."

[1] Compt. rend., 151, 1351 (1910).

Again they say:[1] "The photolysis of the secondary aldehydes (ketones) give carbon monoxide, as those of the primary aldehydes, but are distinguished by the absence of hydrogen. The type of decomposition of ordinary acetone, which decomposes very rapidly into carbon monoxide and ethane

$$CH_3COCH_3 = CO + C_2H_6$$
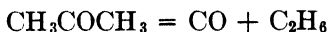
appears to again take place in the higher chain ketones, such as methylnoyl-ketone, $C_{11}H_{22}O$ (liquid), and palmitone, $C_{31}H_{62}O$ (solid), but the hydrocarbons which are formed being liquids or solids, the evolved gas, of which the quantity is moreover very small, is composed solely of carbon monoxide."

Maquenne appears to completely overlook the hydrogen which is evolved when he says: "The ease with which CO is produced in all of the preceding decompositions makes us think that acetone would double its volume, by the discharge, into CO and C_2H_6; the experiment has completely verified that prediction.

"One could not measure the low pressure because of the enormous pressure of the acetone at the temperature of the experiment. The composition of the gas varies little with the pressure, moreover, CO and C_2H_6 always dominating."

de Hemptinne found that the composition of the evolved gases is the same in the presence and in the absence of phosphorus. "This other isomer of allyl alcohol gives under the same conditions:

carbon dioxide	2
hydrocarbon C_nH_{2n}	1.5
carbon monoxide	48.5
hydrogen	11
hydrocarbon $C_2H_6+CH_4$	37

"Acetone appears therefore to decompose first into carbon monoxide and ethane, whereby secondary methane is formed

$$CH_3-CO-CH_3 = C_2H_6 + CO$$

"According to the analysis, allyl alcohol appears to decompose in an entirely different manner than the two isomers, acetone and propyl alcohol, which both decompose in about the same way.

"The constitutional formula of allyl alcohol is $CH_2=CH-CH_2OH$; the hydrocarbon nucleus which contains a double bond, seems therefore to better withstand a physical stress than the analogous nucleus of propylaldehyde C_2H_5-CHO and of acetone $CH_3-CO-CH_3$, in which the oxygen appears to be more tightly bound.

"From the chemical standpoint a nucleus with a double bond is less stable in the sense that it reacts more easily with other elements; moreover, experience teaches that with energetic oxidation, the hydrocarbon splits at the place where the multiple bond occurs. One can therefore draw here the same conclusion as before, namely, that the chemical constitutional formula does not necessarily tell the location of the strongest bond considered from the mechanical standpoint.

"In order to be able to meet all objections, I made several other experiments in another apparatus in the presence of phosphorus and without phosphorus.

	Without Phosphorus	With Phosphorus
carbon dioxide	1.5	2
hydrocarbons C_nH_{2n}	1	1.5
carbon monoxide	30	28
hydrogen	20	17
ethane and methane	47.5	51.5

"One can see from these experiments that the carbon monoxide splits off from the molecule as an entity, because otherwise one would have to find much less carbon monoxide, as was the case with alcohol, in the presence of phosphorus because of the absorption of oxygen."

It would have been interesting if de Hemptinne had given the relative rates of decomposition in the presence and absence of phosphorus.

Poma and Nesti's results are valuable because they showed a complex residue after the decomposition. "We then proceeded to study the effect of the discharge on acetone vapor. In this case the conductivity of the acetone vapor was comparatively high compared with the preceding cases. Keeping all other conditions constant, the intensity of the current which passed was comparatively high. At the same time the luminosity in the ozonizer was also relatively high. On the other hand, the volume of gas produced was small.

"The analysis of the gas was:

CO_2	1.6%
$C_2H_2 + C_2H_4$	5.0
CO	38.1
$CH_4 + C_2H_6$	55.3

"The reaction proceeds in the vapor phase according to the equation:

$$CH_3COCH_3 = CO + C_2H_6$$
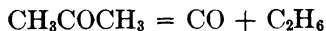
"The distillation residue when redistilled left an oily yellow residue of high density which may contain acetonyl-acetone. Using Knorr's γ diketone reaction, we treated a small portion of the liquid with excess glacial acetic acid and ammonia, boiled for one minute, added dilute sulfuric acid and dipped a pine splint in the boiling solution. The wood was colored deep red. The Ehrlich test also was positive, indicating that the reaction products formed from acetone by the silent discharge contain appreciable quantities of a γ diketone, probably acetonyl-acetone."

The results of Poma and Nesti show that the decomposition of acetone in the discharge is not as simple as Berthelot and Gaudechon found with the quartz mercury lamp. While the principal reaction may result in the formation of CO and C_2H_6, other reactions also occur which give not only different gaseous products but also new compounds in the liquid residue.

Acetic Acid

In the photochemical decomposition of acetic acid, there is fair agreement among the results, with the exception of those of de Hemptinne:

	CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon	41	14	13	32 [*]	—
Maquenne 2 mm.	20.7	33.9	4.5	38.5 [**]	2.4 [****]
'' 50 mm.	11.6	42.6	24.9	19.5 [**]	1.3
'' 100 mm.	9.6	44.6	34.4	11.5 [**]	0.3
Poma and Nesti	35.4	18.5	28.3	17.3	—
de Hemptinne	22	10		18 [***]	50

[*] 13% CH_4; 19% C_2H_6
[**] CH_4
[***] Includes H_2
[****] C_2H_2 and C_2H_4

In the fatty acid series and in passing from the alcohols to the acids, Berthelot and Gaudechon[1] point out the relation between the gaseous product obtained to the composition of the compound.

"The photolysis of the acid group CO_2H is characterized by the predominance of carbon dioxide; it is accompanied by hydrogen and carbon monoxide. In the first members of the normal fatty acid series, $R.CO_2H$, we have pointed out some of the hydrocarbons composed of R_2 as well as methane. That characteristic is found again in the higher chain acids, butyric $C_4H_8O_2$, heptylic $C_7H_{44}O_2$, caprylic $C_8H_{16}O_2$, capric $C_{10}H_{20}O_2$, palmitic $C_{16}H_{32}O_2$, and stearic $C_{18}H_{36}O_2$. As before, when one advances in the series, the evolution of gas decreases while the quantity of gaseous hydrocarbons decreases, then disappearing completely."

They also say:[2] "The acid radical CO_2H is characterized by an abundance of CO_2 which forms 40 to 60 volumes; to this is added 15 to 20 volumes each of CO and H_2.

"When one passes from alcohols to aldehydes and to acids the quantity of hydrogen decreases and that of carbon dioxide increases."

Maquenne[3] postulates two successive reactions to explain his results, although it is simpler to conclude that there are two primary reactions.

"Glacial acetic easily decomposes in the discharge. . . .

"One sees that this body gives birth in the first reaction, to carbon dioxide and methane. These two gases react immediately with each other, as in the experiments of Thenard, and one sees appear a large quantity of carbon monoxide and hydrogen. There are formed also some of the non-volatile polymers which remain at the bottom of the discharge tube."

[1] Compt. rend., **151**, 1351 (1910).
[2] Compt. rend., **151**, 479 (1910).
[3] Bull., **40**, 62 (1883).

Poma and Nesti[1] do not explain the presence of carbon monoxide in the decomposition products. "We also repeated this experiment with acetic acid and obtained a gas with the composition:

CO_2	35.4%
CO	18.5
CH_4, C_2H_6	17.3
H_2	28.3
	99.5%

". . . Since the reaction is more complex, two different causes of the reaction may be considered corresponding to the equations:

(1) $2CH_3CO_2H = 2CO_2 + C_2H_6 + H_2$

(2) $CH_3CO_2H = CH_4 + CO_2$
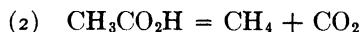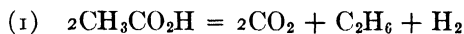
"The liquid remaining in the flask distilled without residue."
Another possible reaction is a breakdown into CO and H_2:

$$CH_3COOH = 2CO + 2H_2$$
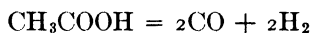
According to this, a volume of hydrogen equal to the volume of carbon monoxide will be formed. If, then, this amount of carbon monoxide is subtracted from the total quantity of hydrogen, there will be left $28.3 - 18.5 = 9.8\%$. The volumes of gases remaining then have a striking relation to the volumes in equation (1).

	% Remaining	Corrected %	% in Equation (1)
CO_2	35.4	56.6	50
$CH_4 + C_2H_6$	17.3	27.7	25
H_2	9.8	15.7	25

de Hemptinne obtained results far different from anyone else. He gives a simple but inadequate explanation.
"Acetic acid gives

carbon dioxide	22%
hydrocarbon C_2H_{2n}	50
carbon monoxide	10
hydrogen and hydrocarbon C_nH_{2n+2}	18

"Acetic acid, $C_2H_4O_2$, appears to give as the first decomposition product $C_2H_4 + O_2$; other explanations are scarcely admissible, because the presence of a large amount of ethylene does not agree with the assumption that CO_2 is separated as an entity."

In the experimental work in this laboratory on methyl alcohol, ethyl alcohol, acetaldehyde, acetone, and acetic acid, results have been secured which in several cases show more clearly the course of the reactions than the results in the work which has been reviewed.

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[1] Gazz., 51 II, 87 (1921).

Apparatus

It has already been pointed out that the apparatus which we used was unique in allowing photochemical reactions with the Tesla discharge to be carried out at high temperatures, although in not every case was this feature utilized.

Our apparatus consisted essentially of four parts; the electrical circuit which generated the high-frequency current; the ozonizer which was comprised of concentric glass tubes through which the vapors and high frequency discharge passed; the flask containing the boiling liquid; the receiving apparatus for collecting the undecomposed vapor and the liquid and gaseous decomposition products.

The electrical circuit is shown in Fig. 3. B represents a 10,000 volt transformer for use on 110 volt A.C. and with a capacity of 250 watts. A repre-
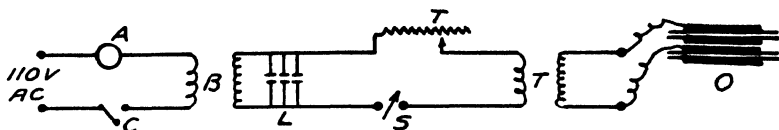
FIG. 3

sents an A.C. ammeter and C a single-pole switch. Three Leyden jars, 15 cm. in diameter and with tinfoil 16 cm. high, are shown at L. S represents a variable spark gap, with zinc terminals. This was placed in a wooden box, tightly covered to confine the ozone and permit less noisy operation. I represents a variable inductance for tuning the primary with the secondary Tesla circuit.

T represents the Tesla coil. There were two turns in the primary and 65 in the secondary. The secondary coil was wound on a wooden frame approximately 22 cm. in diameter and 50 cm. long. This combination of turns was used because it was found by trial to work best with the rest of the circuit. It will be well to emphasize here the importance of correct tuning; it will no doubt be sufficient to state that the number of turns in the Tesla coil and the number of Leyden jars can be selected by trial so that a good discharge will be obtained in a particular discharge tube. If the number of turns is not quite correct, or too many or too few condensers are used, the discharge will be weak. In this regard it is interesting to note the remark of Jackson and Northall-Laurie on tuning (p. 1607).

It was found that the best results were secured by using sufficiently large wire in all parts of the circuit. From the wall plug to the primary of the transformer, ordinary heater cord, No. 18 wire, was used; from the secondary to the Leyden jars, No. 20 bare copper wire; from these condensers to the primary of the Tesla, No. 14 bare copper wire was used. In this part of the circuit conduction is mostly on the surface of the wire and a large diameter is necessary. The secondary of the Tesla coil was of No. 20 annunciator wire, while the primary was No. 14. From the secondary of the Tesla to the discharge tube, No. 22 bare copper wire was used.

All of the electrical apparatus was elevated so that it could not be touched accidentally and the only wires near the apparatus were those from the secondary of the Tesla circuit. Since they carried high frequency current, they were not dangerous.

During operation the terminals of the variable spark gap were from 5 to 8 mm. apart; the current in the 110 volt circuit usually remained at 3.6 amperes, although it varied occasionally from 3.4 to 3.8 amperes.

O represents the ozonizer. The type which was finally found most satisfactory was designed after trials with several different types.

The first ozonizer was something like Fig. 4. Both tubes were of pyrex glass. The diameter of the outer tube was 35 mm. inside, and the outer diameter of the inner tube was 20 mm.
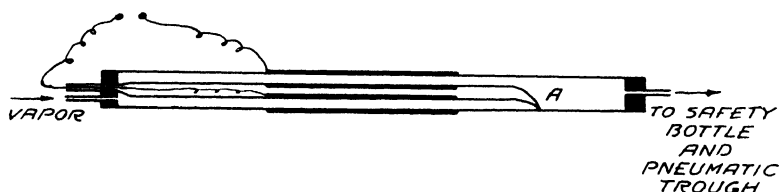
FIG. 4

At A the inner tube was drawn out and sealed and the end was bent down so that it supported the tube exactly in the center of the outer tube.

The coatings (30 cm. long) on the outside of the outer tube and on the inside of the inner tube consisted of copper electroplated on silver. The silver was deposited by Brashear's method, the tubes being first cleaned with a solution of stannous chloride, then rinsed, and then treated with nitric acid, and given a final rinsing with distilled water.

This ozonizer was not perfectly satisfactory because the tubes were too large and the discharge space or distance too great. For that reason, the next ozonizer was constructed with smaller tubes. The new outer tube was 20 mm. outside, and 17 mm. inside. The inner tube was 9 mm. outside. The distance through which the discharge passed was now 4 mm., whereas in the first ozonizer it was 6 mm. The cross sectional area of the discharge space was also smaller, being now about 1.65 sq. cm., where before it had been 3.65 sq. cm. The use of these smaller tubes was satisfactory from the standpoint of having a more restricted space through which the discharge passed. It was actually found that the discharge was more constant and even than before, and that the vapors and gases were swept along better. The rate of decomposition was also higher.

The small size of the tubes, however, made it impossible to use the same arrangement for the entrance of the vapor and for the electrical connection with the coating of the inner tube. A new design was therefore used: At the point where the wire connecting the inner tube passed in there was a free opening so that no difficulty arose from sealing the wire in glass. This arrangement had the distinct advantage of allowing the freest possible passage to the vapor and gases. It had the disadvantage of being somewhat

difficult to construct and of being rather fragile. In the next type these disadvantages were overcome, but before describing the next design, some special problems which were encountered with the small tubes but not encountered when using the big tubes, should be discussed.

Since the new inner tube was so small (only 7 mm. inside) it was almost impossible to first deposit silver on the inner wall and then plate copper on electrolytically. Recourse was had to another method which proved very

FIG. 5

simple and satisfactory. The method depends on the decomposition of copper formate by heating:

$$Cu(HCO_2)_2 = Cu + H_2O + CO + CO_2.$$
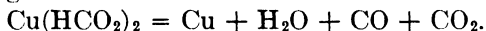
The tube to be plated was filled with copper formate which had been dried at 105° and then powdered in a mortar. The tube so filled was held oblique and heated slowly and carefully over a Bunsen burner. The tube was heated from the top downward to prevent the evolved gases from blowing out the copper formate. If the operation is carefully performed, an even, adherent film of copper is obtained on the glass. The coating on the outer tube was also changed. The tightly adherent silver-copper coating was replaced by a thin copper foil wound on and secured with wire. It is scarcely proper to call this a
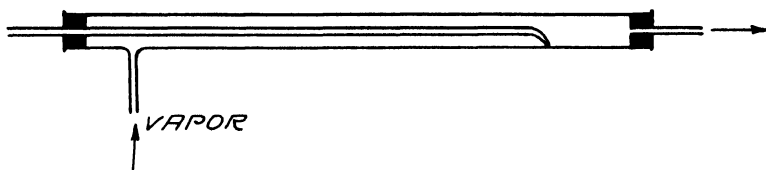
FIG. 6

coating, since it was not in optical contact with the glass. It appeared to work as well as the first coatings and was subsequently changed only by substituting aluminum foil for the copper. The aluminum lasted indefinitely without oxidizing or melting at the operating temperatures.

The next type of ozonizer was somewhat simplified because it was not necessary to seal the inner tube into the outer tube, Fig 6. The end of the inner tube was drawn out and bent as before to hold the tube in the center. The vapor entered through a side arm and the gases had a free exit. This type proved very satisfactory. It was easily made and assembled and quite readily replaced in case of breakage. However, since the breakage in service was rather high, one change was made. A separate tube, 30 cm. long and of the same diameter as the other tube, was provided with a side arm. This short tube was connected to the discharge tube by means of rubber tubing: In case

of breakage of the discharge tube, this short tube could be used again. It eliminated sealing a side arm on each new discharge tube.

With this new design of ozonizer, the copper coating on the inside of the inner tube was abandoned in favor of a bare copper wire, about 7 mm. in diameter, just small enough to slide in the inner tube. This was satisfactory in operation and replacement was very easy.

The side arm from the ozonizer was connected directly to the flask containing the boiling liquid. To provide a steady flow of vapor through the
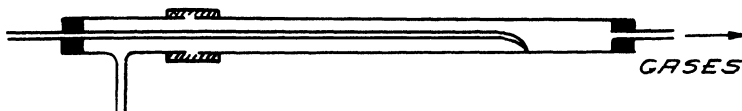
FIG. 7

discharge tube and prevent spasmodic boiling, an ebullator tube was always used in the flask, an electric coil was used for heating, and the flask was protected from drafts with an asbestos cylinder.

For heating the ozonizer a 20-burner gas combustion furnace was used and to insure even heating the outer tube was laid on a layer of asbestos paper. The temperature was measured by means of a thermometer secured to the top of the tube and insulated with several layers of asbestos paper to prevent loss of heat by radiation.
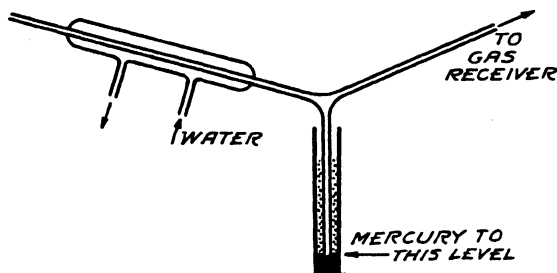
FIG. 8

The receiving end of the apparatus was made as follows:

This arrangement permitted the continuous collection of the gases and liquid without the admission of air. The gases were collected in bottles in a pneumatic trough.

Method of Analysis

The analyses of the gas were made according to the directions given in Dennis' "Gas Analysis," and were briefly as follows:

Gas removed	Solution in Gas Pipette
CO_2	NaOH 1:2
Olefines	15-20% fuming H_2SO_4
SO_3	NaOH 1:2
O_2	alkaline pyrogallol
CO	ammoniacal Cu_2Cl_2
NH_3	5% H_2SO_4

The hydrogen was next taken out by combustion over CuO at a temperature of 270°, and the residue was then burned in a Dennis combustion pipette.

The olefines were treated several times in a pipette containing ammoniacal silver solution in order to remove the acetylene without taking out the ethylene, although Ross and Trumbull[1] have shown that this method is only approximate.

Experimental Results

Methyl Alcohol

Methyl alcohol was decomposed at a temperature of 75°. The outer tube was 18 mm. outside, 15 mm. inside; the inner tube was 6 mm. outside; the coating was 40 cm. long.

The gaseous product consisted only of carbon monoxide and hydrogen in the following proportions:

$$CO \quad 7.5\%$$
$$H_2 \quad 92.5$$

This result indicates that the principal reaction is:

$$CH_3OH = HCOH + H_2$$

The original alcohol contained only a trace of formaldehyde as determined by the method of Georgia and Morales.[2] It was found that the condensate always contained a relatively large amount, and in one particular experiment it contained between 0.5 and 1.0% of formaldehyde. From the volume of hydrogen obtained in this experiment, it was calculated that the condensate should contain 0.75% of formaldehyde. Considering the limit of accuracy of this method of determining formaldehyde, the check of the amount of formaldehyde with the equivalent amount of hydrogen is sufficiently good to conclude that the principal reaction with methyl alcohol is its decomposition into formaldehyde and hydrogen.

It is not difficult to account for the formation of 7.5% of carbon monoxide. It may either be formed from formaldehyde as follows:

$$HCHO = CO + H_2$$
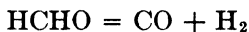
or from methyl alcohol:

$$CH_3OH = CO + 2H_2$$
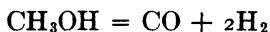
The second reaction was concluded by Jackson and Northall-Laurie to be the principal reaction of methyl alcohol in the decomposition by the high frequency discharge. On the other hand, Russ[3] showed that formaldehyde is decomposed at 150° by the silent electric discharge into CO and H_2, and it was further shown by Löb[4] that formaldehyde plus water vapor under the influence of the silent discharge gives CO and H_2.

Jackson and Northall-Laurie operated under reduced pressure and it is easily possible that, even with the brief discharges which they used, the amount

[1] J. Am. Chem. Soc., **41**, 1180 (1919).
[2] Ind. Eng. Chem., **18**, 304 (1926).
[3] Z. Elektrochemie, **12**, 412 (1906).
[4] Z. Elektrochemie, **11**, 751 (1905).

of energy was so great for the quantity of alcohol present that the primary reaction product, formaldehyde, decomposed into CO and H_2 before the discharge ceased.

It may be concluded, therefore, that the primary photochemical reaction with methyl alcohol is the formation of formaldehyde and hydrogen in every case. A secondary reaction is the formation of carbon monoxide and hydrogen from the formaldehyde.

Our results agree with those of Berthelot and Gaudechon except that they obtained 5% of CO_2. They ascribe this to the reaction between formic acid formed from the alcohol with a small amount of oxygen present in the reaction tube.

The formation of methane found by Maquenne, de Hemptinne, and Jackson and Northall-Laurie is the result of still another reaction. It was found by Brodie[1] that carbon monoxide and hydrogen would give methane and water under prolonged action by the silent discharge. This undoubtedly happened with these investigators. de Hemptinne operated his tube for long periods of time. It has already been shown that Jackson and Northall-Laurie probably had a very high concentration of photochemical energy acting on a small amount of vapor, while Maquenne found that as the pressure in his apparatus decreased, and the amount of energy per unit of weight of vapor thereby increased, the relative amount of methane became greater. It may be concluded, therefore, that one reaction, under suitable conditions, in the discharge tube can be:

$$CO + 3H_2 = CH_4 + H_2O$$
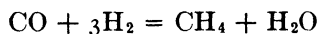
Ethyl Alcohol

Ethyl alcohol was decomposed at temperatures just above the boiling point and at nearly 400°. The results of several experiments checked closely at the same temperature; also at these widely different temperatures very little difference in composition was found:

	85°	380°
$C_2H_2 + C_2H_4$	10.4	10.3
CO	21.6	22.7
H_2	53.8	52.9
C_nH_{2n+2}	14.2	14.1

The mixture of unsaturated hydrocarbons was about 25% ethylene and 75% acetylene.

The outer tube used with ethyl alcohol was 17 mm. outside and 14 mm. inside; the inner tube was 6 mm. outside. The coating was 40 cm. long.

The condensed liquid had the odor of acetaldehyde and readily reduced an ammoniacal silver solution. No quantitative determination of the amount of aldehyde was made.

In the review of the literature on ethyl alcohol, it has been pointed out that probably the chief primary reaction is the formation of acetaldehyde and hydrogen. Another primary reaction is the dehydration of the alcohol to form ethylene and water.

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[1] Ann., **169**, 270 (1873).

It is probable that the formation of carbon monoxide and the saturated hydrocarbons results from the decomposition of the acetaldehyde, and for that reason it will be more interesting to discuss together the reactions of alcohol and aldehyde after giving the results obtained with acetic aldehyde.

The rates of decomposition of ethyl alcohol at 100° and 380° were 16.7 and 83.3 cc. per minute, respectively. The ratio of the reaction velocities over this range is therefore 1.06 per 10°.

Acetaldehyde

Acetic aldehyde was decomposed at several temperatures, ranging from 40° to 340°. The outer tube had a diameter of 19.5 mm. outside and 17.0 mm. inside. The inner tube was 6.1 mm. outside and 4.7 mm. inside. The coating on the outer tube was 27 cm. long, except in the experiment at 40°, where it was 25 cm. The tube was water-jacketed in the experiments made at 40°, 70° and 80°.

Because of some solution of the gases, particularly carbon monoxide, in the condensate on the walls of the reaction tube in the experiments at 40° and 70°, the results cannot be considered to give an accurate picture of the gaseous products at these temperatures. (This probably happened also in some of the previous work where the percentage of carbon monoxide was low—see p. 1625). The results at 40° and 70°, however, do help to show a trend in the proportions of the constituents and for that reason are included here:

	40°	70°	210°	320°
CO_2	2.3	—	—	—
C_2H_2 or C_2H_4	0.0	3.5	1.3	0.3
CO	35.5	46.2	49.8	49.3
H_2	39.4	27.7	16.7	10.8
$CH_4 + C_2H_6$	22.8	22.6	32.1	39.6

At the higher temperatures carbon monoxide comprises about one-half of the gaseous product. It may be concluded that the primary action of the discharge on aldehyde is to split off the CO group in this fashion:

$$H_3C-\underset{\underset{O}{\|}}{C}-H \longrightarrow H_3C + H + CO$$
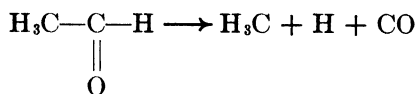
From the H and CH_3 there is either the possibility of the formation of ethane and hydrogen:

$$2CH_3 \longrightarrow C_2H_6$$

$$\text{and} \quad 2H \longrightarrow H_2$$

or the formation of methane:

$$CH_3 + H \longrightarrow CH_4$$
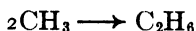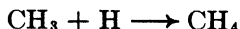
Acetaldehyde may therefore be decomposed in two ways photochemically:

$$2CH_3CHO \longrightarrow C_2H_6 + H_2 + 2CO \qquad (1)$$

$$\text{or} \qquad CH_3CHO \longrightarrow CH_4 + CO \qquad (2)$$
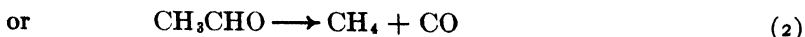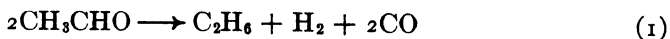
It will be observed that the proportion of the products is not the same at all temperatures, but it is interesting to note that at 210° the volume ratio of $CO:H_2:C_nH_{2n+2}$ is very close to $3:1:2$, a condition which would be true if reactions (1) and (2) occurred to an equal extent:

$$2CH_3CHO = C_2H_6 + H_2 + 2CO$$
$$CH_3CHO = CH_4 + CO$$

$$3CH_3CHO = C_2H_6 + CH_4 + H_2 + 3CO$$
$$\text{or } 3 \text{ vol } CH_3CHO = 3 \text{ vol } CO + 1 \text{ vol } H_2 + 2 \text{ vol } C_nH_{2n+2}$$
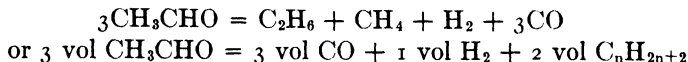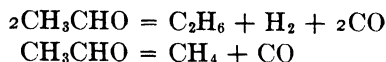
When discussing ethyl alcohol it was pointed out that some of the gaseous decomposition products probably came from the acetaldehyde which was first formed from the alcohol. An interesting relation between the products formed from aldehyde and alcohol may now be observed. Because the first reaction in the decomposition of alcohol is the formation of acetaldehyde, it would be expected not only that the products obtained would be the same but that the ratio of CO to C_nH_{2n+2} when decomposing alcohol would be the same as when decomposing pure acetaldehyde. The relation is actually close if the results at 210° are used:

	CO	C_nH_{2n+2}	CO/C_nH_{2n+2}
CH_3CHO (210°)	49.8	32.1	1.55
C_2H_5OH (85°)	21.6	14.2	1.53
C_2H_5OH (380°)	22.6	14.1	1.60

The hydrogen cannot be included in this ratio because there is not complete decomposition of the aldehyde which is formed from alcohol. Because reaction (2) of acetaldehyde begins to predominate at higher temperature, this ratio will of course change as the temperature rises.

One of the most interesting features in the photochemical decomposition of alcohol and acetaldehyde is that the composition of the gaseous decomposition product of alcohols is practically the same at low and high temperatures, while with acetaldehyde it is different. With acetaldehyde, two reactions occur to more or less equal extent at low temperatures, while at high temperatures, one reaction tends to predominate. There are two explanations but we believe that this fact is most probably evidence of depolarization by heat.

The first explanation is that when decomposing alcohol, the alcohol vapor in the discharge tube may absorb most of the photochemical energy in the wave-lengths which are necessary to decompose aldehyde. The fact that the rate of decomposition of alcohol is only one-third that of aldehyde shows that the total energy required for decomposition is greater for alcohol than for aldehyde.

If the wave-lengths absorbed by the alcohol are those which would decompose the aldehyde, a close connection between these photochemical reactions and contact catalysis can be pointed out. Bancroft[1] has cited a case which may be considered an interesting analogy.

[1] J. Phys. Chem., **27**, 853 (1923).

"Copper and nickel do not behave alike towards alcohol at the same temperature. Though both tend to convert alcohol into acetaldehyde and hydrogen, nickel is much more likely to decompose the aldehyde into carbon monoxide and methane. . . . . The specific effect occurs also during hydrogenation, though the difference is not so marked. . . . . Armstrong and Hilditch consider that both alcohol and water are adsorbed selectively by copper, thus decreasing the adsorption of the aldehyde and protecting it from decomposition."

That alcohol may absorb the wave-lengths which are needed for the decomposition of aldehyde would explain the slower rate of decomposition of aldehyde and might explain the change in the proportion of gaseous products of aldehyde as the temperature changes.

The second explanation of the change in products seems more nearly true. Bone and Smith[1] found that at 400°, acetic aldehyde rapidly decomposes almost completely into methane and carbon monoxide. That the photochemical reaction also tends to go this way as the temperature is raised indicates very clearly that the molecule becomes more instable in this direction. In the introduction it was postulated that the action of heat as a depolarizer would be shown by an increased rate of reaction and a higher so-called temperature coefficient as the temperature of thermal decomposition is approached. We are now able to conclude that the action of heat as a depolarizer in a photochemical reaction may be demonstrated in two ways.

First, at higher temperatures, one reaction tends to predominate; this reaction will be that one in the direction of which the higher temperature has brought about the more instable molecule.

Second, the rate of reaction increases as the temperature rises.

It has already been shown that as the temperature rises, the change in the composition of the gaseous decomposition products indicates depolarization by heat. The rates of reaction also show clearly that depolarization occurs with acetaldehyde; that at temperatures approaching the thermal decomposition point, light has less work to do in decomposing the molecule.

Temperature	80°	210°	320°	340°
cc./min.	156	168	194	236

(A blank run at 380° without the discharge gave 7.5 cc./min; there was no evolution at 340° or below).

A calculation of the ratio of the reaction velocities at 10° intervals shows the same effect:

Temperature	Rate in cc./min.	K
80°	156	
210°	168	1.006
320°	194	1.010
340°	236	1.10

[1] J. Chem. Soc., **87** II, 910 (1905).

A corollary of these conclusions is that if the temperature of thermal decomposition is not approached, the composition of the gaseous decomposition products will not change over a wide change in temperature. This may be demonstrated by both ethyl alcohol and acetic acid. These two substances begin to decompose thermally at $500°$[1] and about $800°$,[2] respectively, or at temperatures not approached in our tube. The fact that alcohol gives the same products at $85°$ and at $380°$ is an indication of the truth of this corollary; on the other hand, this evidence cannot be considered as absolute proof because in a heated glass tube alcohol decomposes in the same two ways in which it decomposes photochemically. The thermal decomposition products of acetic acid are not mentioned. Further work should be carried out in connection with this interesting question.

Fig. 9

Acetone

The decomposition of acetone was carried out in one of the early tubes. The diameter of the outer tube was 35 mm., of the inner tube 20 mm., and the length of the coating 25 cm. Because the tubes were larger than in the later designs, the rate of decomposition can not be directly compared with the other substances which have already been discussed.

At $80°$, 22 cc. of gas were formed in 5 minutes, or at a rate of 4.4 cc. per minute. The gaseous products analyzed as follows:

Acetylene and olefines	4.1
CO	49.6
H_2	19.1
C_nH_{2n+2} (principally CH_4)	27.2

This result is most nearly like that of de Hemptinne. All investigators have agreed that the primary reaction is the splitting off of CO, but only Berthelot and Gaudechon and Poma and Nesti have explained the reaction further. The former obtained only ethane and carbon monoxide in essentially equal amounts, hence the explanation is simple; the latter obtained no hydrogen but found the condensate to be complex.

In the present work, no analysis was made of the condensate. Because CO comprises one-half of the gaseous product and methane and hydrogen both are formed from the CH_3 group, it must be true that either free carbon or a carbon-rich compound is formed in the decomposition of acetone. Since
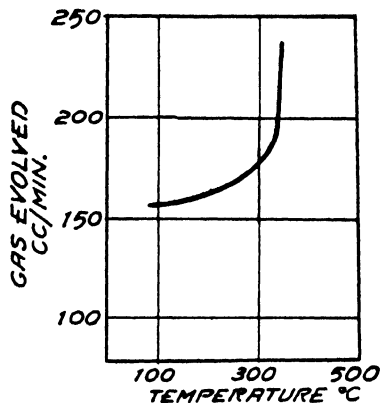
[1] Berthelot and Jungfleisch: "Traite elem. de Chimie Org.," 2nd Ed., **1**, 256 (1886).

[2] Berthelot: Ann. Chimie, (3) **33**, 300 (1851).

no free carbon was observed, it must therefore be concluded that a carbon-rich compound is formed. It is possible that this compound is a polymerized olefine.

Sabatier and Senderens[1] found that acetone is decomposed in the presence of nickel at 270° to give a little carbon monoxide, ethane and ethylene, but principally methane, hydrogen and carbon.

Acetic Acid

In the decomposition of acetic acid the gaseous products, as with ethyl alcohol, have practically the same composition at low and high temperatures:

Temperature	118°	320°
CO_2	13.3	15.3
C_2H_2 or C_2H_4	3.5	3.1
CO	36.4	35.8
H_2	26.7	23.5
$CH_4 + C_2H_6$	20.1	22.3

These results do not conform to those obtained in any previous work except in that of Maquenne. Berthelot and Gaudechon obtained a predominance of carbon dioxide; so also did Poma and Nesti. de Hemptinne found a large amount of ethylene.

The significance of obtaining the same products at low and high temperatures has already been pointed out when discussing acetaldehyde.

It seems quite evident that in our apparatus the principal reaction cannot be:

$$CH_3COOH = CH_4 + CO_2$$
$$or \quad 2CH_3COOH = C_2H_6 + 2CO_2 + H_2$$
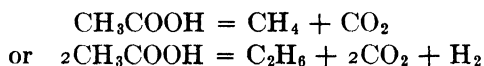
Because of the large amount of carbon monoxide, it is more probable that the principal primary reactions are:

$$2CH_3COOH = 2CO + C_2H_4 + 2H_2O$$

(with polymerization of the excess ethylene)

$$and \quad CH_3COOH = 2CO + 2H_2$$

The so-called temperature coefficient of the photochemical decomposition of acetic acid is higher than that of ethyl alcohol. At 118° the rate of decomposition is 31 cc. per minute; at 320° it is 200 cc. per minute. The so-called temperature coefficient is therefore 1.10 for 10°. Although the curve for the change in rate of decomposition was not obtained with acetic acid, one might judge from this rather high coefficient that the slope might change even more rapidly than with acetic aldehyde when the temperature of thermal decomposition is approached.

Ethylene and Acetylene

It seemed possible that in several of our photochemical decompositions there occurred a polymerization of ethylene or acetylene because after con-

[1] Ann. Chim. Phys., (8) 4, 474 (1905).

tinual use of a discharge tube, there was some deposit of a gummy or semi-hard, brown or black substance. Other workers have described polymerization products of acetylene or ethylene.

Berthelot and Gaudechon[1] placed acetylene in a "tube subjected to the action of the lamp of 110 volts for 1 hour at 2 cm. distance, 1 hour at 5 cm., 1 hour at 8 cm. Initial volume 2.6 cc. Final volume 2.18 cc. Contraction 16%. At the end of some moments, one observes a fog appear in the tube, which is then desposited on the surface of the mercury, and a solid layer on the walls of the tube, the thickness increasing progressively, which shows the colorations of thin plates. The chemical action, at first very rapid, soon slows down, as a result of the non-transparency of the deposit to ultra-violet rays.

"The deposit is of a brownish yellow color, and has the particular odor of the polymers of acetylene obtained by the action of the silent discharge on the gas.

"There is no liquid benzene. The residual gas is entirely absorbed by ammoniacal copper chloride. Polymerization has therefore occurred without decomposition.

"The preceding chemical action, like those which are related to the ionization of the gas, is assisted by the diminution in pressure which renders the gases better conductors. This is equalized by the addition of an inert gas, which diminishes the partial pressure of the active gas in the mixture."

In another experiment Berthelot and Gaudechon[2] used ethylene alone in a "tube subjected to the action of the 220 volt lamp at 4 cm. distance, during 2 hours. Initial volume 2.72; final volume 2.42. Contraction 11%. One part of the residual gas is analyzed by combustion, then by the addition of alkaline pyrogallol.

	Total Gas	CO_2 Formed	Contrac- tion	O Con- sumed	Resi- due
Observed	1.25	2.48	2.50	3.74	0.01
Calculated for C_2H_4	1.24	2.48	2.46	3.72	0.00

"The residual gas is therefore pure ethylene. There is formed a waxy liquid polymer which gives off a rancid fat odor, and boils at a little above 100°. It is a substance which recalls caprylene or the homologous compounds obtained in the pyrogenic decomposition of wax.

"In another experiment, after 3 hours exposure at about 5 cm. distance from the 110 volt lamp, ethylene contracted 13% with the formation of the same polymer. The residual gas, analyzed as before, is pure ethylene.

"The ease and simplicity of the reaction caused by ultra-violet rays contrasts with the previous negative results of Goriarnoff and Bontleroff, who state in their paper 'Sur les polyolènes': 'We have endeavored to polymerize ethylene but without succeeding.'"[3]

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[1] Compt. rend., **150**, 1170 (1910).

[2] Loc. cit. p. 1171.

[3] **Ann.**, **169**, 147 (1873).

When Berthelot and Gaudechon[1] subjected a mixture of acetylene and ethylene to the action of their ultra-violet lamp, they imply that the two gases polymerized separately.

"The tube was exposed for 2 hours to the rays from the 220 volt lamp at a 4 cm. distance. Initial volume 3.22, composed of 1.55 cc. C_2H_2 plus 1.70 cc. C_2H_4. Final volume 2.36 cc. Contraction 26%.

"The quartz tube is coated with a solid brownish yellow layer, of identical appearance to the polymer of acetylene, and besides, some of a fatty layer which can be distilled off above 100°, in the form of a heavy vapor of rancid odor and having an odor similar to the product of the condensation given by ethylene alone."

Several attempts have been made to polymerize acetylene and ethylene separately by the silent discharge. P. and A. Thénard[2] found that in the silent discharge ethylene alone condenses to a powerfully odorous liquid, soluble in ether, insoluble in water. M. Berthelot[3] reported that ethylene gives a little acetylene, some hydrogen and resinous condensation products. Wilde[4] condensed ethylene to a liquid and acetylene finally to a brown, brittle solid.

M. P. E. Berthelot[5] found that ethylene condenses rapidly but since the time of action in his apparatus was generally 24 hours, it is not clear just how rapidly the condensation occurs. During the action of the silent discharge a little acetylene and benzene are formed and considerable hydrogen. The condensed liquid had the formula $C_2H_{3.4}$. He reported also that acetylene condenses very rapidly, first to a liquid and then to a solid. In the residual gas he found hydrogen, ethylene and a trace of benzene.

Losanitsch and Jovitschitsch[6] stated that under the action of the silent discharge, ethylene polymerizes into a yellow, viscous liquid with a very strong, somewhat pleasing odor. The liquid boils above 200° and its formula is $(C_2H_4)_n$.

Jovitschitsch[7] later published more work on the probable structure of the polymerization products of acetylene and ethylene. He concluded that the probable formula of the first is $C_{30}H_{26}$ and of the second, $C_{30}H_{54}$.

Collie[8] subjected a mixture of ethylene and carbon monoxide (80:20) to the silent discharge and after several hours obtained 2.5 grams of liquid. He separated three fractions boiling from 50° to 180° and the fourth fraction, boiling above 180°, was a brown, sticky substance resembling burnt india-rubber, and when heated, it smelled like rubber. Some of the residual gas was hydrogen. Collie concluded that the ethylene was condensing more easily than the carbon monoxide, although aldehyde were formed to a slight extent, so his next experiment was with ethylene alone. After submitting

[1] Loc. cit. p. 1171.
[2] Compt. rend., **76**, 1513 (1873).
[3] Bull., (2) **26**, 103 (1876).
[4] Ber., **7**, 357 (1874).
[5] Compt. rend., **126**, 567 (1898).
[6] Ber., **30**, 135 (1897).
[7] Monatshefte, **29**, 1, 5 (1906).
[8] J. Chem. Soc., **87**, 1540 (1905).

ethylene to the discharge for several hours, he found the residual gas to be hydrogen. He collected four fractions, boiling from $-100°$ to $250°$ and a resin boiling above $250°$. He found the maximum amount of distillate between $133°$ and $170°$ and another increase above $200°$. The resin represented two-fifths of the whole of the substances produced.

Collie found that the percentage of hydrogen gradually fell from 16.0% (C = 83.4) in the first fraction to 12.3% (C = 87.7) in the distilled resin. He concluded "that ethylene gas under the influence of the silent electric discharge at the ordinary temperature not only unites with carbon monoxide, but also polymerizes, yielding a series of complicated hydrocarbons having a boiling point approximating to that of hydrocarbons having the formula $C_{10}H_{20}$; moreover, this molecule loses hydrogen and in its turn polymerizes, yielding a substance possessing properties somewhat like those of india-rubber and a composition very near to $(C_5H_8)_x$."

From all of these results it may be concluded that both ethylene and acetylene do polymerize to form gummy substances. It seemed to us particularly an interesting question whether a mixture of acetylene and ethylene in polymerizing formed two polymers of the separate gases or a polymer which would have the formula $(C_4H_6)_n$.

Experimental Work

We found that, when ethylene alone is run through the discharge tube, there is gradually formed on the walls of the tube a liquid which is at first colorless, then yellow, then brown. Most of this substance can be removed with benzene, but there still remains a more or less hard, yellow or brown substance which becomes soft under the benzene treatment but does not dissolve immediately. Most of this hard substance is on the inner tube of the ozonizer.

No quantitative determination was made of the composition of these polymers of ethylene.

In the first experiments with a mixture (50-50) of acetylene and ethylene a tube with a coating 45 cm. long was used. The rate of flow of gas was 50 cc. per minute. The formation of the yellow or brown polymer could be observed after a few minutes of operation and after building up continually for an hour the deposit on the inside of the outer tube was about 1 mm. thick. The maximum thickness was at a distance of about 30 cm. from the front end of the coating.

If the discharge continued much longer than one hour, the thickness of the deposit became so great at this point that the discharge began to concentrate here and became more intense. The brown polymer then started to carbonize, the discharge concentrated still more and very soon the tube cracked or a hole formed in it and a spark discharge occurred.

It is not perfectly clear why the deposit reached a maximum at 30 cm. from the front end of the coating. The distribution of the deposit was like this:

at 20 cm. the deposit began,
at 30 cm. the deposit was thickest,
at 40 cm. the deposit ended.

It is believed that polymerization starts in the first part of the discharge and continues as the gases pass through the tube with the formation of higher boiling point polymers. The polymers with a sufficiently high boiling point are probably formed after traveling about 30 cm. through the tube and therefore condense at this point. This decreases, at this particular place, the distance which the discharge has to travel and the discharge gradually becomes a little more intense here, although it was perfectly uniform in the beginning. Once started, the effect becomes more pronounced as the experiment continues.

If the rate of flow of the gas mixture was made less, e.g., 30 cc. per minute instead of 50, the deposit occurred over a longer portion of the tube and a maximum was not so evident. As a practical means of overcoming this difficulty when measuring the amount of contraction, the coating was shortened from 45 to 15 cm.

It was found that either a very intense discharge or a combination of the discharge and heat would cause decomposition of the polymerized substance. On the inside of the outer tube, the deposit was a thick, yellow, sticky liquid. On the other side of the inner tube where the discharge per unit of area was greater than on the outer tube (17:7), the liquid deposit gradually blackened and charred. If the temperature of the tube was raised above 200°, the polymer began to carbonize very rapidly on the outer tube also. It was found that if no external heat were applied, the temperature naturally rose to about 190° and remained at that point.

Rate of Flow versus Contraction

In this experiment, the inner tube was 7 mm. (outside), the outer tube was 17 mm. (inside), and the coating was 15 cm. long. The temperature was 190°. A 50-50 mixture of acetylene and ethylene was passed through.

Rate, cc./min.	% Contraction
32	68
36	67
51	56
65	55
254	23
448	6

If these are plotted, the curve indicates that maximum contraction with zero flow will be somewhat less than 100%. In other words, some gas other than the original ethylene and acetylene is formed to the extent of about 10-20%. This is interesting because the exit gases were found to contain hydrogen to the extent of about 8% at the lower rate of flow.

The ratio of acetylene to ethylene was quite different in the exit gases from their ratio at the beginning. Before passing through the tube, they were present in equal parts. After passing through the discharge tube, there was present three to four times as much ethylene as acetylene. This fact seems to indicate that the two gases polymerize separately and that acetylene polymerizes more readily than ethylene.

However, analysis of the resinous, gummy, semi-liquid deposit which appeared to be a mixture of polymers having boiling points from about 150° to 250°, showed the formula to be very close to $(C_4H_6)_n$.

Several attempts were made to further polymerize this thick liquid.

(1) A small amount of the liquid was treated with a few drops of quinoline. There was no change either in the cold or on heating. After remaining at 140° for five days there was no change in the consistency.

(2) The liquid was kept in a sealed tube at 140° for 5 days. There was no change.

(3) The liquid was kept in a sealed tube with sodium amalgam at 50°. The amalgam was introduced in an atmosphere of nitrogen and had a clean
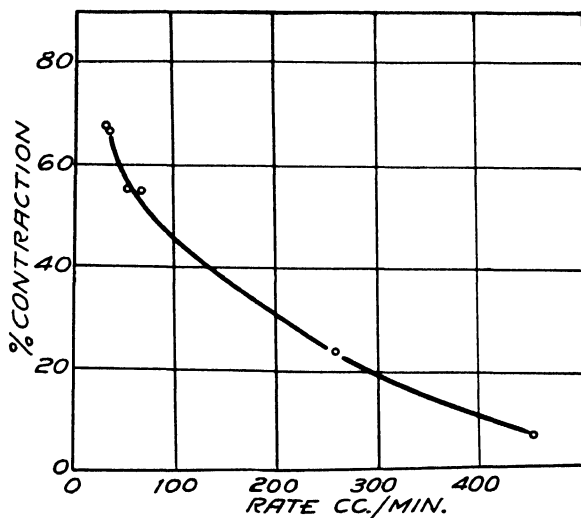
FIG. 10

surface. There was no change in two days, but after five days there were flecks of a brown solid on the side of the tube with unchanged liquid still remaining.

(4) There was no change in the liquid kept in contact with the clean surface of sodium for two days at 50°.

In this report on the action of the Tesla discharge on ethylene and acetylene, the curve showing the relation of contraction to rate of flow is probably the most interesting material presented. It suggests at once the possibility of obtaining and isolating in a fairly pure condition the separate fractions of the polymers by using a short discharge space and a suitable rate of flow.

Sulfur Trioxide

An interesting photochemical synthesis seemed to us to be the formation of sulfur trioxide from sulfur dioxide and oxygen. Findlay[1] stated that a

[1] Z. Elektrochemie, 12, 129 (1906).

mixture of SO_2 and O_2 will give some SO_3 under the influence of the Tesla discharge. Losanitsch[1] using the silent discharge, found that SO_2 alone gives SO_3 and free sulfur quite rapidly. Berthelot[2] and Wilde[3] also studied the action of the silent discharge on the oxidation of SO_2 by O_2.

According to the experiments of Coehn[4] and Coehn and Becker,[5] SO_2 is split by ultra-violet light into SO_3 and S, and SO_2 and O_2 give SO_3. They later concluded after further work with a quartz mercury lamp that a definite photochemical equilibrium exists. At 160°, for example, the equilibrium mixture contains 65% SO_3. They found the temperature coefficient to be 1.2 per 10° between 50° and 160°.

Moser and Isgarischeff[6] studied the action of the silent discharge on a mixture of SO_2 and O_2 and on SO_3 alone. They operated at temperatures from 50° to 70° in order to prevent the condensation of SO_3. In the experiment on SO_3 alone, they used nitrogen saturated with about 20% of SO_3. They could detect no decomposition into SO_2 and O_2 but concluded that free sulfur and a superoxide, S_2O_7, are formed. They concluded that the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is irreversible:

"By the use of stoichiometric mixtures of SO_2 and O_2 (2:1) the formation of the superoxide by condensation of the SO_3 occurs only after the necessary union of the gases to form SO_3.

"In the presence of an excess of oxygen occurs the further oxidation of the SO_3 which has been formed, to sulfur peroxide in the sense of the Berthelot equation:[7]

$$2SO_3 + \tfrac{1}{2}O_2 = S_2O_7$$
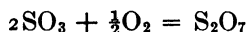
"In the presence of an excess of SO_2 occurs a condensation of that substance with the separation of sulfur and the formation of SO_3 according (compare Losanitsch and Jovitschitsch:)[7] to the equation:

$$3SO_2 = 2SO_3 + S$$

"As soon as the sulfurous acid is used up according to this equation there occurs, with a further separation of sulfur, the formation of sulfur peroxide."

Some of their results are given in the following table. Their maximum yield in grams per KWH was 14.3.

Apparatus 2. Composition of gas: 61.5% SO_2, 32.4% O_2; 6.1% N. T 67°.

Volts	Milli-amps	Watts	Speed of Flow, cc./min.	SO_3 Formed, Grams	Time, Minutes	SO_3, Gm./KWH
12500	1.92	11	0	0.0102	15	3.5
12500	2.9	16.5	7.3	0.0560	27	7.4
12500	2.8	16	21.8	0.0298	8	14.3

[1] Ber., **40**, 4657 (1907).
[2] Compt. rend., **86**, 20 (1878).
[3] Ber., **7**, 357 (1874).
[4] Z. Elektrochemie, **13**, 545 (1907); Chem. Ztg., **31**, 541 (1907).
[5] Z. physik. Chem., **70**, 88 (1910).
[6] Ber., **40**, 4656 (1807).
[7] Compt. rend., **86**, 20 (1878).

Experimental Work

In our apparatus we used a considerably higher rate of flow than Moser and Isgarischeff and obtained higher yields per KWH. The outer tube used for this experiment was 18 mm. outside and 15 mm. inside; the inner tube had a diameter of 6 mm. outside. The coating on the outer tube was 40 cm. long.

A mixture of 2 volumes of sulfur dioxide and 1 volume of O_2 was passed through the tube with the following results:

Rate cc./min.	Average Temp.	In Exit Gas		SO_2 oxidized $\times$ 100 SO_2 original	Yield gms./KWH
		gms. SO_2	gms. SO_3		
329	300°	2.220	0.773	21.8	23.4
1218	300°	4.480	0.982	14.9	59.5

It is unfortunate that these experiments could not have been carried further. It is probable that if several other values had been obtained, varying the rate of flow, a curve which would indicate the point of equilibrium would have resulted. One thing is worth while noting in these two experiments. The difference in the rate of flow is large but the difference in the percentage of SO_2 oxidized to SO_3 is rather small. Also, with the faster rate of flow, the yield per KWH is higher. Both of these facts indicate that the reaction takes place very rapidly. An apparatus in which the discharge would pass only through the unchanged mixture, or in other words, an apparatus in which the discharge would be used most efficiently, would probably give higher values for the amount of SO_2 oxidized and very much higher yields per unit of energy used.

Summary

(1) An apparatus has been designed in which photochemical reactions can be carried out by means of a Tesla discharge at temperatures up to 350° to 400°. The range could be extended by using quartz or glazed porcelain tubes instead of pyrex glass.

(2) The reactions in the Tesla discharge give essentially the same products as other photochemical energy sources. Exactly the same results are not obtained, possibly because any given wave-length or band may not be present to the same extent.

(3) There has been obtained evidence that a compound can be made photosensitive by means of heat. That a compound is made photosensitive is shown by the increased rate of reaction and the higher temperature co-efficient.

(4) Regardless of the photochemical reactions which occur at low temperatures, the predominant photochemical reaction at temperatures approaching the thermal decomposition point is that reaction which results from the instability of the molecule brought about by the high temperature.

(5) The developed apparatus seems a good one in which to try out the possibilities of influencing the reactions by using a second substance, e.g., mercury, in the discharge tube.

(6) The gaseous and some of the liquid decomposition products of methyl alcohol, ethyl alcohol, acetone, and acetic acid have been determined. Some of them have been of service in drawing the conclusions just mentioned under (2) and (3).

(7) A gummy resin has been obtained in the polymerization of a mixture of acetylene and ethylene. This appears to be a mixture of polymers of the two separate gases and not polymers of a combination of the two. Several methods of further polymerizing this resinous mass were tried but in none of these trials was there any further polymerization.

This work was suggested by Professor Bancroft. It is a pleasure and a privilege to be able to thank him, in this way, for his constant interest, criticism, suggestions and inspiration.

Cornell University.

A NEW EQUATION FOR THE RATE OF FORMATION OF THE PHOTOGRAPHIC LATENT IMAGE*

BY JULIAN M. BLAIR AND PHILIP A. LEIGHTON

Introduction

An equation which, based upon theoretical postulates, would correctly express the relation between the rate of formation of a developable image and the time and intensity of exposure on photographic emulsions would be of value for the information it might give regarding the nature of the process forming the latent image.

Several equations which express a relationship between these quantities have been presented, and have been excellently summarized by Ross,[1] who has also added one of his own. However, these equations either do not fit the experimental data closely, or are not based on theoretical postulates, or both. The research here reported was undertaken with the view of finding an equation which would overcome these difficulties. In the earlier equations, trouble has been caused by the "reciprocity failure," or lack of inverse proportionality between intensity and time of exposure. In order to avoid this complication we have, in the present work, considered the effect of time of exposure only, while using a uniform light intensity.

The Rate of Formation of the Latent Image in Very Thin Emulsions

Hurter and Driffield[2] showed that the density of a photographic plate is proportional to the mass of silver per unit area. Accordingly, the density of a plate, when developed under such conditions that all developable silver halide grains have been reached and reduced by the developer, will be a measure of the extent to which the reaction forming the latent image has progressed.

Ordinary commercial photographic plates are so opaque, due to the concentration of silver salts, that grains of silver halide on the side of the emulsion facing the incident light receive greater exposure than grains buried deeper in the emulsion.[3]

If after exposure and development the density of such a plate is determined it will not be an accurate measure of the degree of developability at any layer of the emulsion, but rather a summation of the different degrees of developability at the various levels.

In order to overcome this difficulty, we used in this research a special thin emulsion in which the amount of silver halide was so small that the plates

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[1] F. E. Ross: "The Physics of the Developed Photographic Image," Eastman Kodak Co. Monograph No. 5, p. 48 (1924).

[2] F. Hurter and V. C. Driffield: Photography, 1890, August 30.

[3] Ross: Loc. cit., p. 40.

were quite transparent before development, and grains at different levels of the emulsion could be exposed very nearly equally.

Measurement of the density of the special plates before development showed that the amount of silver halide per unit area was constant along lines parallel to the shorter dimensions of the plate, but along lines parallel to the longer dimensions there was a uniform increase in density from one end of the plate to the other. In order to avoid error from this source, the plates were cut into two longitudinal strips, which were reversed in the plate holder so that whenever the dense portion of a strip was given a certain exposure the correspondingly less dense portion of the other strip was given the same exposure. The average density of the two was accepted as the true value of the density.

In order to expose the strips, tungsten lamps burning at constant voltage, were placed behind a ground glass in a ventilated box. On the opposite side of the ground glass an opening in the box was covered with a No. 50 Wratten laboratory filter. This filter transmits a band between 4000 and 5000 Å, with a maximum transmission around 4550 Å.

Two and one-half meters in front of the box an ordinary camera plate holder was rigidly mounted in this beam of uniform blue light. As stated, the strips were mounted with ends reversed in this plateholder. The slide of the plateholder was then drawn so that one half inch of the ends of the strips were exposed. After 15 seconds the slide was drawn an additional half inch. This was repeated until the whole of the plate was exposed, each half inch of plate receiving 15 seconds more exposure than the next. On some plates, part of the exposures were of still greater duration, so that the whole range of sensitivity of the plates was explored.

Different plates were found to be coated with slightly different amounts of silver halide. Error from this source was avoided by making the greatest exposure on one pair of strips and the least exposure on the next pair of strips. This permitted the densities of all plates to be determined in terms of the amount of silver halide on the first plate.

The strips were developed for 20 minutes at a temperature of 19°C. in the Ferrous Oxalate Developer described by Hurter and Driffield,[4] then fixed, washed, and dried in the usual manner. This developer was chosen because it gives a high density, i.e., develops a maximum number of exposed grains, yet has very little tendency to spread and affect unexposed grains. It should be pointed out that some later publications in giving the formula for this developer leave out the bromide, which was described by Hurter and Driffield, and the use of which is essential.

The densities of the various parts of the plates were measured with a Burt photoelectric cell. This cell was mounted in one end of a dark box, separated by a partition from a tungsten lamp operated at constant voltage in the other end. The plates to be measured were placed over an opening in the partition, the size of which could be adjusted to the size of the section of plate to be measured. A water cell was placed between the lamp and the plate.

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[4] F. Hurter and V. C. Driffield: Phot. J., **38**, 76 (1898).

The photoelectric cell was connected in series with a 45 volt battery, a condenser, and a charge and discharge key. The key was placed in the charge position for a measured interval of time, then it was thrown into the discharge position and the accumulated charge passed through a ballistic galvanometer of high sensitivity. Comparisons between this photoelectric method and a surface thermopile method gave concordant results for density.

The circles on Fig. 1 represent the developable densities produced by various times of exposure under the conditions described. The abscissa is
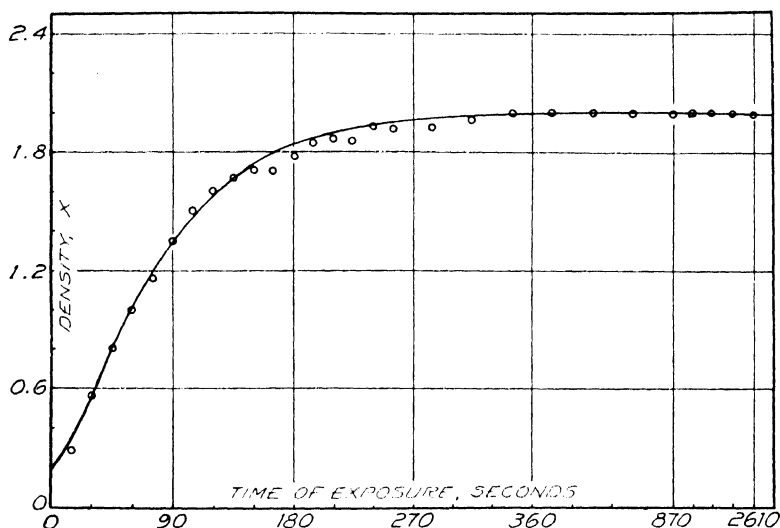
FIG. 1
Time-Density Relations for Thin Emulsions
Circles = observed; Solid line = calculated

time of exposure rather than the conventional log time. No correction is made for "fog." The distance along the time axis for the points t = 805; 1305; 1740; 2175; and 2610 seconds, respectively, are shortened to avoid extension of the graph.

The Ideal Maximum Density

In the analysis which is to follow we use a concept which we shall call the ideal maximum density. By this we mean the density that the plate would attain if all of the silver halide present in the plate had been converted during development into metallic silver.

Jones and Hall[5] have shown that even at optimum exposure to light of moderate or low intensity this value is never attained. However, by assuming the relation as demonstrated by Hurter and Driffield[6] that the density of a plate is proportional to the mass of silver per unit area, it is possible to determine the ideal maximum density by chemical means.

In the determination of this value, a plate was cut into four longitudinal strips of precisely equal area. Two alternate strips were exposed to the blue

[5] L. A. Jones and V. C. Hall: Proc. Int. Cong. Phot., 7, 115 (1928).
[6] F. Hurter and V. C. Driffield: Photography, loc. cit.

light previously mentioned long enough to produce the maximum developable density for this light. These two strips were then developed with the standard developer, fixed, and washed. Without drying, they were immersed in hot sodium hydroxide solution for 24 hours. The residual silver was then filtered off and washed free from gelatine, dissolved in nitric acid, and the silver precipitated as the chloride and weighed in the usual manner.

The two remaining strips of the plate were, without any previous treatment, immersed in hot sodium hydroxide solution for 24 hours. At the end of that time the silver oxide was filtered off and the silver content determined as before. From the relative amounts of silver chloride produced in the two cases the ratio between the ideal maximum density and maximum developable density was determined. The ratio found was 1.095. When applied to the maximum developable density shown in Fig. 1, the ideal maximum density for the plates and development conditions used is found to be 2.19.

Derivation of An Equation for Developable Density

In attempting an analysis of the rate of formation of the latent image, as indicated by the developable density produced, we have been led to five basic postulates, as follows:

1. *The process of formation of the latent image is chemical.* The idea that it probably consists of the photochemical liberation of minute amounts of free metallic silver has received support from the work of many investigators.[7]

2. *Two processes are involved, one a forward reaction, tending to produce the latent image, and the other a reverse reaction, tending to destroy it, or to change the developable grains into their original condition.*

The phenomenon of reversal or solarization is an old and well established fact. The new aspect here presented is that reversal begins as soon as the first grains have been rendered subject to development, and is concurrent with the formation of the latent image. We have obtained direct experimental evidence in support of this assumption, which will be presented in another paper.

3. *The forward reaction is autocatalytic.* This is suggested by the shape of the density-time curve, as well as by the effect of "flash" exposures and by the sensitizing effect of silver on emulsions.

4. *The forward reaction is a function of the number of grains in the original state.* This is a general property of photochemical reactions where light absorption is weak.

5. *The reverse reaction is a function of the developable density.* It is reasonable to assume that the rate of the reverse reaction, which decreases the number of developable grains, is some function of their concentration, and therefore a function of the developable density.

[7] Abegg: Archiv Wiss. Phot., I, 268 (1899); Brit. J. Phot., **46**, 196 (1899); Lüppo-Cramer: "Kolloidchemie und Photographie" (1908); Lorenz and Hiege: Z. anorg. Chem., **92**, 27 (1915); Sheppard and Trivelli: Phot. J., **61**, 403 (1921); Fajans: Chem. Ztg., **45**, 666 (1921).

Proceeding on the basis of these postulates, we can say that the rate of formation of the latent image, dx/dt, will be governed by the relation:

$$dx/dt = f_1(x) \cdot f_2(b\text{-}x) - f_3(x) \tag{1}$$

where x = the developable density, b = the ideal maximum density, and t = time of exposure to light of constant intensity. Accordingly, $f_1(x)$ represents the autocatalytic term, $f_2(b\text{-}x)$ the term expressing the relation between the forward reaction and the number of grains in the original state, $b\text{-}x$, and $f_3(x)$ represents the dependence of the reverse reaction on the number of developable grains.

The autocatalytic reaction appears to be proportional, not to x, but to the square root of x, i.e., $f_1(x) = K_1 x^{\frac{1}{2}}$. The other two functions, since the grains are mutually independent, should involve no more than a direct proportionality. Accordingly, we obtain the equation:

$$dx/dt = K_1 x^{\frac{1}{2}}(b\text{-}x) - K_2 x. \tag{2}$$

This equation is found to predict the slope rather accurately for all values of x. In order to evaluate the constants K_1 and K_2, the ratio K_1/K_2 was found by considering a point on the curve at which maximum density has been attained. At this point $dx/dt = 0$, $x = 2.0$ and $b = 2.19$. This gives the ratio

$$K_1/K_2 = 7.45$$

By employing this ratio, when other measured values for dx/dt and the corresponding values for x are substituted in the equation, the constant values $K_1 = 0.0122$ and $K_2 = 0.00164$ are found.

The differential equation (2) may be integrated, and for the determined values of the parameters it yields the relation:

$$e^{K_1 t \sqrt{\left(\frac{K_2}{2K_1}\right)^2 + b}} \cdot C = \frac{\sqrt{\left(\frac{K_2}{2K_1}\right)^2 + b} + x^{\frac{1}{2}} + \frac{K_2}{2K_1}}{\sqrt{\left(\frac{K_2}{2K_1}\right)^2 + b} - x^{\frac{1}{2}} - \frac{K_2}{2K_1}} \tag{3}$$

where C is the constant of integration, and possesses the value 2.125.

This value of C was determined by substituting corresponding values of x and t for any one point shown in Fig. 1. Using this value of C in the above equation, the values of x predicted for various values of t were determined. The resulting curve is shown by the continuous line in Fig. 1. Within limits of error, it is in agreement with the experimental curve throughout the whole region of exposures we have thus far investigated.

Instead of the usual form of density-time curve, with a considerable "foot" or flat underexposure portion, this curve, both experimental and calculated, has a very short foot, and moreover, strikes the ordinate (zero time) at a density of 0.2.

This is due in part to the fact that no fog correction was made in either the calculation or measurement of x, and in part to the scale of the abscissa, time instead of log time. The thinness of the emulsion must also be a contributory cause of the short foot, since the grains deep in the emulsion receive full exposure and become developable as rapidly as those near the surface. No solarization was observed experimentally and none would be predicted for the values of the parameters found.

Summary

A differential equation, based on definite theoretical postulates, which expresses the relation between density and time of exposure in photographic emulsions, has been presented. Measurement of the density-exposure relationships on very thin emulsions shows that the equation accurately reproduces the experimental values.

THE BEHAVIOUR OF THE TUNGSTIC ACIDS TOWARDS SODIUM HYDROXIDE

BY ARTHUR M. MORLEY

In a previous publication[1] the preparation of four types of tungstic acid has been described. Preparations of each type were subjected to various ageing processes, and from a combined analytical and X-ray study of the original and aged products, deductions were made as to the structure of the various tungstic acids. The present publication describes experiments which were carried out to study the action of solutions of sodium hydroxide upon tungstic acid products of the above mentioned types, with special reference to solubility, and the production of colloidal solutions.

A search of the literature reveals the fact, that although there are many references of a general nature to the solubility of tungstic acids in sodium hydroxide, no systematic work has been carried out on this subject, and no quantitative data are available. It is generally agreed, however, that one of the chief characteristics of tungstic acid is the ease with which it dissolves in solutions of the strong alkalies, giving perfectly clear solutions. Since in the experiments carried out by the author it was desired to study the peptisation of the tungstic acids, the sodium hydroxide solutions employed were, in most cases, of low concentration.

Experimental

Preparations.

All the preparations employed were made from solutions of ammonium tungstate and hydrochloric acid, as described in detail in a separate paper.[1] The analyses and general characteristics of the preparations are as shown in Table I.

A pure primrose-yellow tungsten trioxide was also prepared, by heating a tungstic acid of type A in a platinum basin for three hours at 800°C. in an electric furnace.

All preparations were sieved through a 90 mesh I.M.M. sieve.

In the paper previously referred to, the structures of the tungstic acids employed were shown to be as follows: Type A—H_2WO_4, H_2O; Type B— a hydrated amorphous variety of either H_2WO_4 or H_2WO_4, H_2O; Type C— a mixture, consisting chiefly of an imperfectly crystallised or a condensed acid, with smaller amounts of H_2WO_4 and amorphous tungstic acid; Type D —H_2WO_4.

[1] Morley: J. Chem. Soc., 1930, 1987 T.

TABLE I

Type A			Type B		
	I	II		I	II
WO$_3$	85.49(%)	85.48(%)	WO$_3$	84.10(%)	84.12(%)
H$_2$O	14.39	14.41	H$_2$O	15.14	14.67
NH$_3$	0.01	0.02	NH$_3$	0.01	0.02
Cl	Nil	Nil	Cl	Trace	Trace
	99.89	99.91	Insoluble matter*	0.78	1.07
				100.03	99.88

	Type A	Type B
Colour	Lemon yellow	Greyish white
Appearance under microscope (× 800)	Flat leaflets exhibiting frequent twinning. Largest about 10μ in length, and 4μ across the centre. May be regarded as crystalline	Glassy amorphous particles of irregular shape. Size very variable. Maximum breadth between 2μ and 50μ

Type C			Type D	
	I	II	WO$_3$	91.16(%)
WO$_3$	89.69(%)	90.00(%)	H$_2$O	8.38
H$_2$O	9.56	9.18	NH$_3$	0.05
NH$_3$	0.77	0.74	Cl	Trace
Cl	Trace	Nil		99.87
	100.02	99.92		

	Type C	Type D
Colour	Greenish yellow	Deep yellow
Appearance under microscope (× 800)	Amorphous. Very small, almost spherical particles, of average diameter 1 μ	Identical with Type C products

* Matter insoluble in water after fusion with sodium carbonate. Due to absorption of calcium from tap water used for washing the precipitated tungstic acid.

General Method.

The general method employed was to mix suitable quantities of sodium hydroxide solution and tungstic acid, in a flask coated internally with paraffin wax, which was then fitted with a waxed cork and suspended in a large water thermostat at 25° C. ± 0.1°C. The contents of the flasks were shaken periodically, and were examined and analysed at intervals, by determining the total amount of tungsten in the supernatant liquids, and in the liquids after ultra-filtration through collodion membranes. The difference between the values so obtained was regarded as a measure of the amount of tungstic acid present in the colloidal condition. One series of experiments was carried out with tungsten trioxide and tungstic acid D, but two series were performed with products A, B, and C, the separate preparations used being referred to as I and II in the analyses. The second short series served to confirm the first

set of results, and in addition, certain other determinations were carried out viz. the determination of the pH values of the solutions, and the examination of the solid phase in a selected number of cases.

Experimental Technique.

(a) *Alkali solutions.* The specially distilled water employed for the experiments had a specific conductivity of ca. 2×10^{-6} reciprocal ohms. The sodium hydroxide solution was prepared by subjecting pure metallic sodium to the action of water vapour in an enclosed space, free from carbon dioxide. The saturated solution produced was diluted with freshly prepared conductivity water in the usual type of enclosed apparatus, waxed internally,
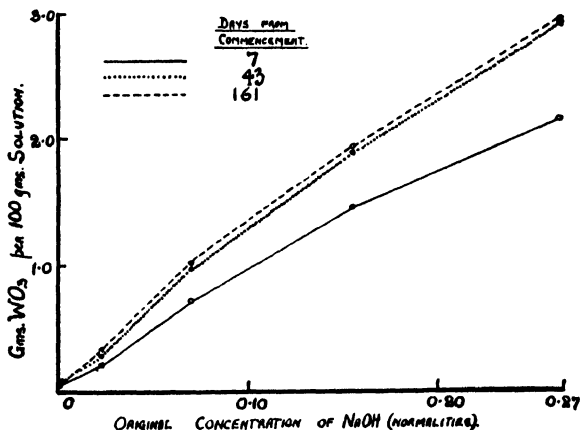
FIG. 1

Tungsten Trioxide in NaOH
Before Ultrafiltration

and with burette attached. This stock solution was diluted as required to prepare the solutions for the experiments.

(b) *Determination of hydrogen ion concentration.* The standard potentiometric method was used. The limit of accuracy of the apparatus employed may be regarded as ± 0.02 of a pH unit. Both the hydrogen and quinhydrone electrodes were used, but since in certain cases at low pH values poisoning of the hydrogen electrode occurred,[1] the values given in the tables are those obtained with the quinhydrone electrode, which behaved normally throughout the investigations.

(c) *Ultrafiltration.* The method of ultrafiltration through collodion membranes was that previously described by Collins and Wood.[2] Tests by Bechold's method[3] showed that the filters held back particles with diameters greater than $1 \ \mu\mu$. It was shown by direct adsorption tests with pieces of collodion membrane and solutions containing tungstate, metatungstate, and

[1] Cf. Britton: J. Chem. Soc., 1927, 147(T); 1930, 1249T.

[2] J. Chem. Soc., 121, 1122 (1922).

[3] Z. physik. Chem., 60, 257 (1907).

colloidal tungstic acid, that there is no adsorption of ions or colloidal particles containing tungsten, by the membranes. It was also shown by quantitative tests on the ultrafiltration of optically void solutions of sodium tungstate, and sodium metatungstate of known tungsten content, that at laboratory temperature, with ultrafiltrations carried out up to two hours, the experimental error due to evaporation of the solutions etc. was not greater than 2%. All ultrafiltrations were carried out under the above mentioned conditions.
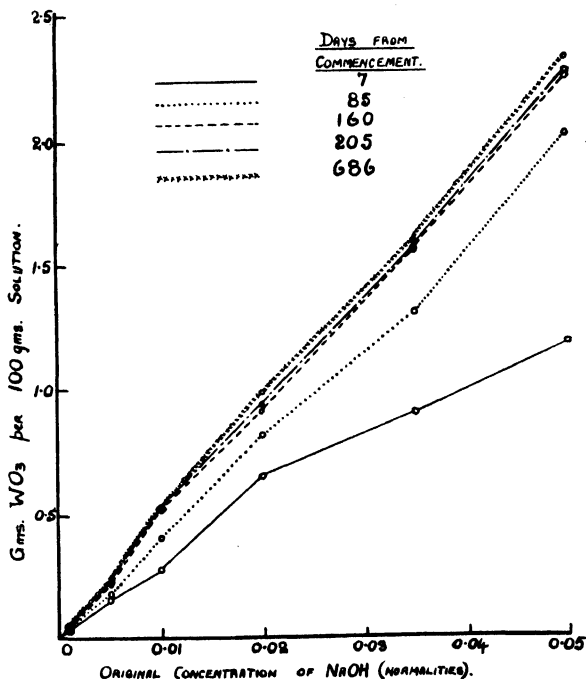
FIG. 2

Tungstic Acid (type A)—in NaOH
Series I—Before Ultrafiltration

(d) *Estimation of Tungsten.* All analyses were carried out by the standard gravimetric mercurous nitrate method. The method was carefully tested, and shown to be accurate with tungsten in the forms of sodium tungstate, sodium metatungstate, and tungstic acid in the colloidal condition. Since small quantities of solutions had to be used in many cases, all portions for analysis were accurately weighed out, and all results were expressed as grams of WO_3 per 100 grams of solution.

All estimations were carried out in duplicate. In all Series I experiments, portions of the solutions were taken for analysis by allowing the solids present to settle for several days and carefully pipetting off the supernatant liquids. Filtration of the solid had been found to be unsatisfactory in many cases, owing to its finely divided nature. The settling method of necessity involved a slight concentration error caused by drops of condensed liquid on the upper portions of the flasks.

This was avoided in the various Series II experiments, a centrifuge then being available. The standard method for obtaining a sample was to shake up the contents of a flask, centrifuge a portion for 30 minutes at 2,000 revs. per minute, and pipette off and weigh part of the supernatant liquid. The centrifuging was carried out in an asbestos box at a temperature of 25° C. ± 0.5° C., so that there was no appreciable change in temperature when the solution was transferred from the thermostat to the centrifuge.

(e) *The solid phase.* Wo. Ostwald[1] and von Buzagh[2] by their work on the "solid phase" rule have shown that generally, in a colloidal system, the amount of substance peptised is dependent on the amount of solid phase present. The author has shown by special tests, that this effect applies to the peptisation of tungstic acid by sodium hydroxide. For this reason, the exact quantities of solution and solid used have been given in the following tables.

Analytical Results

All columns of figures headed WO_3 refer to grams of WO_3 per 100 grams of solution. This also applies to the "Colloid content."

The pH values are those obtained with the quinhydrone electrode on solutions which had been centrifuged in the manner previously described. The ratio WO_3/Na_2O gives an approximate idea of the type of tungstate (e.g. whether normal or metatungstate) present in solution; the WO_3 values are those determined in 100 grams of the final ultrafiltrates, divided by its molecular weight, and the Na_2O values, that present in grams in 100 c.c. of the original sodium hydroxide solution divided by its formula weight. Since the densities of the solutions involved are near unity, it is not necessary to introduce the values for the purpose of these calculations. If sodium be adsorbed by the solid phase, it follows that the WO_3/Na_2O ratio will not accurately represent the composition of the salts in solution.

The colloid contents are given to the second place of decimals. Figures of greater accuracy would be meaningless, as, assuming an ultrafiltration error of 2%, even the figures in the second decimal place may be slightly incorrect.

Graphs are given showing the relation between the concentration of the original sodium hydroxide, and the WO_3 in solution before ultrafiltration, in the tungsten trioxide series, and the Series I experiments for tungstic acids A, B, and C. (Tables I, II, IV, VI).

Tungsten Trioxide

No. of flask	1	2	3	4	5
Conc. or original NaOH (Normalities)	0.001	0.020	0.078	0.157	0.261
Wt. of WO_3 (gms.)	3.0	3.0	5.0	10.0	10.0

In all cases 500 c.c. of alkali were used.

[1] Kolloid-Z., **41**, 163; **43**, 227, 249 (1927).

[2] Kolloid-Z., **41**, 169 (1927); **46**, 178 (1928).

TABLE I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 1) WO₃	pH	After ultra-filtration WO₃	Colloid Content	$\dfrac{WO_3}{Na_2O}$	Appearance of Solution
1	7	0.038	5.42	0.017	0.02	—	
	4	0.068	5.91	0.046	0.02	—	Faintly opalescent
	161	0.063	6.28	0.048	0.015	4.1	
2	7	0.215	9.83	0.216	Nil	—	
	43	0.286	6.97	0.284	Nil	—	Clear
	161	0.320	6.85	0.326	Nil	1.4	
3	7	0.733	12.0	—	—	—	
	43	0.987	7.51	—	—	—	Clear
	161	1.020	7.33	—	—	1.1	
4	7	1.482	12.23	—	—	—	
	43	1.905	7.82	—	—	—	Clear
	161	1.934	7.63	—	—	1.1	
5	7	2.146	12.77	—	—	—	
	43	2.920	11.87	—	—	—	Clear
	161	2.972	8.04	—	—	0.98	

No change was observed in the appearance of the solid phase.

Tungstic Acid—Type A

	Series I						Series II		
No. of flask	9	10	11	12	13	14	25	26	27
Conc. of NaOH (N)	0.001	0.005	0.010	0.020	0.035	0.050	0.010	0.020	0.028
Volume of solution (c.c.)	200	200	150	100	100	100	500	500	500
Wt. of tungstic acid (gms.)	1.0	1.0	1.0	1.5	3.0	4.0	5.5	9.5	10.5

TABLE II

Series I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 2) WO$_3$	After ultra-filtration WO$_3$	Colloid Content	Appearance of Solution
9	7	0.035	—	—	Solutions
	85	0.039	0.006	0.03	9–13
	160	0.041	0.030	0.01	very
	205	0.049	0.038	0.01	slightly
	686	0.044	0.033	0.01	opalescent
					at
10	7	0.160	—	—	commencement
	85	0.187	0.134	0.05	of
	160	0.221	0.208	0.01	experiments.
	205	0.226	0.212	0.01	later
	686	0.228	0.218	0.01	becoming
					clear
11	7	0.282	—	—	Solution 14
	85	0.411	0.388	0.02	clear
	160	0.518	0.523	Nil	throughout
	205	0.527	0.519	0.01	the
	250	0.517	0.519	Nil	experiments
	686	0.518	0.519	Nil	
12	7	0.646	—	—	
	85	0.821	0.782	0.04	
	160	0.919	0.920	Nil	
	205	0.938	0.930	0.01	
	250	0.952	0.939	0.01	
	686	0.979	0.987	Nil	
13	7	0.891	—	—	
	85	1.303	1.267	0.04	
	160	1.565	1.560	Nil	
	205	1.565	1.535	0.03	
	250	1.600	1.604	Nil	
	686	1.594	1.594	Nil	
14	7	1.171	—	—	
	85	2.015	2.031	Nil	
	160	2.238	—	—	
	205	2.262	2.219	0.04	
	686	2.324	2.334	Nil	
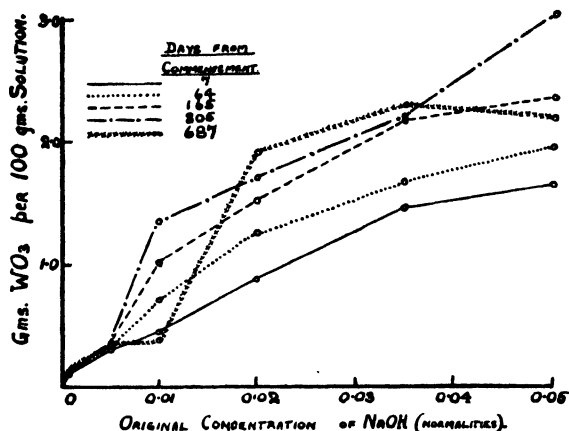
FIG. 3
Tungstic Acid (Type B)—in NaOH
Series I—Before Ultrafiltration

TABLE III
Series II

| No. of flask | Days from start | Before ultra-filtration | | After ultra-filtration | Colloid | $\frac{WO_3}{Na_2O}$ | Appearance |
		WO_3	pH	WO_3	Content		of Solution
25	91	0.455	5.64	0.424	0.03	—	
	161	0.469	4.85	0.457	0.01	—	
	218	0.468	4.46	0.477	Nil	4.0	
26	13	0.601	—	0.561	0.04	—	All
	63	0.854	—	0.766	0.09	—	solutions
	91	0.922	5.41	0.880	0.04	—	resembled
	161	0.937	4.63	0.939	Nil	—	9–13 in
	218	0.954	4.29	0.950	Nil	4.1	Series I
27	91	1.156	5.89	1.072	0.08	—	
	161	1.299	4.96	1.239	0.06	—	
	218	1.317	4.59	1.301	0.02	4.0	

No change was observed in the appearance of the solid phase in either series. The final quantitative results were very similar for both series.

Tungstic Acid—Type B

	Series I						Series II		
No. of flask	15	16	17	18	19	20	28	29	30
Conc. of NaOH (N).	0.001	0.005	0.010	0.020	0.035	0.050	0.020	0.035	0.045
Volume of solution (c.c.)	200	200	150	100	100	100	500	400	400
Wt. of tungstic acid (gms.)	1.0	1.5	2.0	3.0	4.0	5.0	10.0	12.0	12.0

TABLE IV

Series I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 3) WO₃	After ultra-filtration WO₃	Colloid Content	Appearance of Solution
15	7	0.100	—	—	Slight
	64	0.105	0.072	0.03	opalescence,
	165	0.112	0.107	0.005	decreasing
	205	0.104	0.091	0.01	with time
	687	0.125	0.114	0.01	
16	7	0.296	—	—	
	64	0.331	0.269	0.06	
	165	0.352	0.337	0.015	Same as 15
	205	0.346	0.334	0.01	
	687	0.351	0.342	0.01	
17	7	0.456	—	—	
	64	0.714	0.612	0.10	
	165	1.007	0.930	0.08	Same as 15
	205	1.348	1.319	0.03	
	687	0.382	0.371	0.01	
18	7	0.880	—	—	
	64	1.250	1.198	0.05	
	165	1.506	1.418	0.09	Same as 15
	205	1.690	1.569	0.12	
	687	1.900	1.894	0.01	
19	7	1.478	—	—	
	64	1.674	1.644	0.03	
	165	2.129	1.930	0.20	Clear
	205	2.164	1.931	0.23	
	687	2.277	2.250	0.03	
20	7	1.631	—	—	
	64	1.942	1.904	0.04	
	165	2.312	2.173	0.14	Clear
	205	3.018	2.971	0.05	
	687	2.148	2.114	0.03	
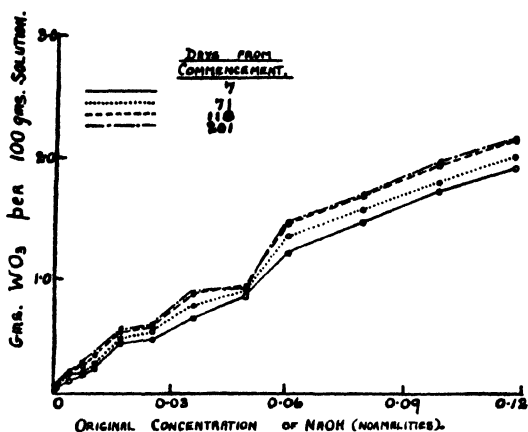
FIG. 4

Tungstic Acid (Type C)—in NaOH
Series I—Before Ultrafiltration

TABLE V

Series II

No. of flask	Days from start	Before ultra-filtration		After ultra-filtration	Colloid Content	$\dfrac{WO_3}{Na_2O}$	Appearance of Solution
		WO_3	pH	WO_3			
28	87	1.147	3.65	1.107	0.04	—	
	170	1.236	2.73	1.145	0.09	—	Clear
	226	1.244	2.79	1.105	0.14	4.8	
29	15	1.282	—	1.239	0.04	—	
	65	1.377	—	1.354	0.02	—	
	87	1.578	5.42	1.565	0.01	—	Clear
	170	2.057	2.87	1.829	0.23	—	
	226	2.081	2.79	1.873	0.21	4.6	
30	87	1.397	6.41	1.282	0.12	—	
	170	1.888	5.75	1.671	0.22	—	Clear
	226	1.805	5.92	1.761	0.04	2.9	

The following changes in the solid phase were observed: in Series I, solid 15 was definitely yellow after 5 days, the remaining solids being unchanged. As time progressed, solids 16-19 slowly changed to a dull yellow colour, but no change in structure was visible under the microscope. After about 90 days, the solid in flask 20 consisted of small white crystals (hexagonal plates) of $Na_2WO_4, 2H_2O$, and unchanged tungstic acid.

These observations were confirmed generally in Series II, e.g., white hexagonal crystals appeared in flask 30.

Tungstic Acid—Type C

Series I

This series actually consisted of three separate short series, the results being combined for convenience. The flasks, therefore, are not numbered consecutively.

No. of flask	44	45	46	39	47	48
Conc. of NaOH (N)	0.001	0.004	0.007	0.010	0.017	0.025
Volume of Solution (c.c.)	200	200	200	150	100	100
Wt. of tungstic acid (gms.)	1.0	1.0	1.0	1.0	1.5	1.5

No. of flask	40	41	21	22	23	24
Conc. of NaOH (N)	0.035	0.049	0.059	0.079	0.098	0.118
Volume of Solution (c.c.)	100	100	50	50	50	50
Wt. of tungstic acid (gms.)	2.0	2.0	2.0	2.0	2.0	2.0

TABLE VI

No. of flask	Days from start	Before ultra-filtration (v. Fig. 4) WO_3	After ultra-filtration WO_3	Colloid Content	Appearance of Solution
44	7	0.047	—	—	
	71	0.058	0.006	0.05	
	118	0.065	0.012	0.05	
	201	0.064	0.026	0.04	Colloidal in appearance;
45	7	0.113	—	—	bluish white by reflected
	71	0.145	0.095	0.05	light,
	118	0.173	0.120	0.05	reddish-orange
	201	0.186	0.119	0.07	by transmitted light
46	7	0.164	—	—	
	71	0.189	0.155	0.03	
	118	0.229	0.164	0.065	
	201	0.254	0.170	0.08	

TABLE VI (Continued)

No. of flask	Days from start	Before ultra-filtration (v. Fig. 4) WO$_3$	After ultra-filtration WO$_3$	Colloid Content	Appearance of Solution
39	7	0.209	—	—	
	71	0.244	0.187	0.06	
	118	0.325	0.238	0.09	
	201	—	—	—	
47	7	0.414	—	—	Colloidal in
	71	0.481	0.398	0.08	appearance;
	118	0.529	0.421	0.11	bluish-white
	201	0.545	0.435	0.11	by reflected
					light,
48	7	0.472	—	—	reddish-
	71	0.523	0.488	0.035	orange by
	118	0.555	0.572	Nil	transmitted
	201	0.575	0.563	0.01	light
40	7	0.632	—	—	
	71	0.728	0.707	0.02	
	118	0.834	0.843	Nil	
	201	—	—	—	
41	7	0.801	—	—	
	71	0.860	0.849	0.01	Clear
	118	0.900	0.894	0.01	
	201	0.890	0.866	0.02	
21	7	1.185	—	—	
	71	1.352	1.321	0.03	Clear
	118	1.451	1.312	0.14	
	201	1.456	1.420	0.04	
22	7	1.447	—	—	
	71	1.562	1.542	0.02	Clear
	118	1.665	1.525	0.14	
	201	1.677	1.636	0.04	
23	7	1.696	—	—	
	71	1.767	1.747	0.02	Clear
	118	1.910	1.799	0.11	
	201	1.933	1.882	0.05	
24	7	1.881	—	—	
	71	2.000	1.936	0.06	Clear
	118	2.118	2.007	0.11	
	201	2.124	2.040	0.08	

Series II

No. of flask	31	32	33	34
Conc. of NaOH(N)	0.010	0.040	0.060	0.080
Volume of solution (c.c.)	500	400	400	400
Wt. of tungstic acid (gms.)	3.3	8.0	8.0	10.8

TABLE VII

No. of flask	Days from start	Before ultra-filtration		After ultra-filtration WO$_3$	Colloid Content	$\dfrac{WO_3}{Na_2O}$	Appearance of Solution
		WO$_3$	pH				
31	93	0.193	6.32	0.161	0.03	—	⎫
	170	0.293	5.95	0.232	0.06	—	⎬ Colloidal
	226	0.324	5.99	0.261	0.06	2.2	⎭
32	93	0.709	6.69	0.707	Nil	—	⎫ Very
	170	0.853	6.67	0.831	0.02	—	⎬ faintly
	226	0.890	6.54	0.881	0.01	1.9	⎭ opalescent
33	14	0.876	—	0.843	0.04	—	⎫
	64	0.957	—	0.933	0.02	—	⎪
	93	0.961	7.10	0.938	0.02	—	⎬ Clear
	170	1.139	6.95	1.119	0.02	—	⎪
	226	1.164	6.96	1.161	Nil	1.7	⎭
34	93	1.318	7.10	1.288	0.03	—	⎫
	170	1.499	7.08	1.436	0.06	—	⎬ Clear
	226	1.471	7.11	1.439	0.03	1.6	⎭

The solid in flask 44 remained pale greenish yellow; the remaining solids of Series I, and all those of Series II changed rapidly to bluish white products.

In both series, approximately similar quantitative results were obtained up to a concentration of initial alkali of 0.05 N. Above this concentration, the values for the total WO$_3$ in solution were higher for Series I than for Series II.

Tungstic Acid—Type D

Owing to shortage of time, only one series of experiments was carried out with tungstic acid D.

No. of flask	69	70	71	72
Conc. of NaOH(N)	0.001	0.005	0.010	0.060
Volume of solution (c.c.)	500	500	500	500
Wt. of tungstic acid (gms.)	5.0	5.0	5.0	12.0

TABLE VIII

No. of flask	Days from start	Before ultra-filtration WO₃	Before ultra-filtration pH	After ultra-filtration WO₃	Colloid Content	$\dfrac{WO_3}{Na_2O}$	Appearance of Solution
69	6	0.038	4.29	0.006	0.03	—	Colloidal in appearance; bright yellow by reflected light, reddish-orange by transmitted light
	27	0.045	4.09	0.014	0.03	1.2	
70	7	0.253	4.19	0.147	0.11	—	
	27	0.270	4.10	0.183	0.09	3.2	
71	7	0.502	4.24	0.370	0.13	—	
	27	0.519	4.14	0.395	0.12	3.4	
72	7	1.915	6.03	1.836	0.08	—	Very slightly opalescent
	27	2.004	6.17	1.980	0.02	2.8	

The solids in flasks 69–71 remained unchanged throughout the experiments. The tungstic acid in flask 72, however, slowly changed to a white solid. The X-ray examination of this product has been described in the previously mentioned publication.

In certain cases, after the final analyses, the solids were taken out of solution, pressed between filter papers to remove excess liquid, and air-dried to constant weight on porous tiles. The following results were obtained:

TABLE IX

Type	No. of flask	Loss on ignition (%)	Loss on ignition (%) of original tungstic acid
A	25	14.41	A. 14.43
	27	14.17	
B	28	11.46	B. 14.69
	29	12.30	
C	31	10.25	C. 9.92
	33	9.78	
D	72	9.24	D. 8.43

Discussion

A study of the pH values of the various solutions, obtained a few minutes after commencing each series, showed that neutralisation of the alkali had taken place, probably producing Na_2WO_4. Thus, the experiments described really record the solubility of the tungstic acids in sodium tungstate solution. With anhydrous tungsten trioxide, the sodium hydroxide was only neutralised slowly, except in the most dilute solution, when immediate "neutralisation"

occurred, this suggesting that adsorption was the original cause of the removal of alkali from the solutions. The soluble sodium tungstate produced would then slowly attack the tungstic acid present, forming salts with increasingly large tungsten content.

The peptisation of tungstic acid by alkali may be conveniently explained by the theory of Zsigmondy, which was worked out in detail in connection with the stannic acids. If sodium hydroxide is added to tungstic acid, sodium tungstate will be produced, and if it is assumed that the tungstate ion is strongly adsorbed by the tungstic acid particles, the latter will become negatively charged. If sufficient charging is effected by this process, dispersion of the particles will result, and a sol will be produced. Alternatively, one may assume that tungstate is formed on the surface of the tungstic acid particles. Dissociation of the product so formed may occur, the sodium ions diffusing into the liquid, leaving the particles negatively charged. The final result of such processes is to produce charged micelles containing water, some form of tungstic acid or oxide, and probably sodium, together, of course, with free sodium ions. A study of the colloid contents of the various series shows that with a given tungstic acid, and increasing sodium hydroxide concentration, the colloid content frequently increases from a small value to a maximum, and then decreases. This is particularly well shown in the colloid contents for Types B and D. The effect would be anticipiated, on the following grounds: very small quantities of alkali will produce small quantities of tungstate, and the adsorption of the tungstate ion will charge the particles, but not sufficiently to cause peptisation. Medium quantities of alkali will produce sufficient salt to finally bring about dispersion of the tungstic acid, whilst higher alkali concentrations will finally lead to a coagulation effect on the tungstic acid. It must also be noted that at and above a certain concentration, disintegration of the solid phase occurs, producing molecular tungstate and metatungstate solutions.

The maximum concentration of sodium hydroxide which produced immediate peptisation with the various products was as follows: WO_3, 0.001 N; tungstic acid A, 0.035 N; B, 0.020 N; C, 0.035 N; with D, colloidal matter was present in all solutions tested, i.e. up to 0.06 N. On general grounds, it would be expected that little peptisation would occur with ignited tungsten trioxide, owing to the complex structure and dense nature of the particles. Also, the crystals of tungstic acid A, and the comparatively large glassy particles of tungstic acid B are not suitable products for extensive sol formation. Tungstic acids C and D being of a more finely divided nature and possessing greater adsorptive power than the previously mentioned products (shown e.g. by their ammonia contents), are far more likely to peptise when treated with alkali. These general deductions are in harmony with the observations given in the various Tables under "Appearance of Solution."

During prolonged experiments of the type described in this paper, there are many variable factors, so that the prediction of the possible behaviour in any particular case becomes very difficult. The following possible sources of variation may be considered:—

(a)   Change in the dispersion medium may occur owing to the early formed sodium tungstate passing through various intermediate stages to metatungstate, and possibly still higher polytungstates (v. WO_3/Na_2O ratios. Table V, 28 and 29.).   This will probably cause varying adsorption of the ion containing tungsten, by the solid phase. This tungstate-metatungstate change is shown by the decrease in the pH values of the solution, and the condition of the final ultrafiltrates is approximately indicated by the WO_3/Na_2O ratios. Solutions of tungstic acid C were exceptional, in that the pH values remained relatively high.   This is accounted for by the fact that the solubility of C was rather low, and therefore only incomplete formation of metatungstate would take place.

A study of the solubility "curves" shows that speaking generally, a condition of equilibrium was approached with tungstic acids A and C, and with tungsten trioxide.   Abnormalities were observed with product B whilst D had not sufficient time to attain equilibrium.   Since A and D are essentially definite compounds, it would be anticipated that the products would easily dissolve in sodium hydroxide, and would finally attain an equilibrium.   The much lower solubility of product C is one of the facts which most strongly suggests that it might contain a condensed acid, as previously suggested.[1]   Such a product would not readily be attacked by reagents, and one would expect its solubility in sodium hydroxide to be less than the solubilities of H_2WO_4, H_2O or H_2WO_4.

(b)   Change in the solid phase.   Possible ageing effects are (1) a general coarsening of amorphous particles to larger amorphous particles or (2) crystallisation, either partial or complete.

The evidence (observations and Table IX) shows that such changes were slight with tungstic acids A and C, and not of large extent with D, but were much more pronounced with B.   This greyish white product frequently changed to a yellow substance.   The author has shown by X-ray analysis[2] that such changes are due to crystallisation into H_2WO_4 or H_2WO_4, H_2O or into a mixture of these products.   Also, it was shown by centrifuging, that a tungstic acid B from a solubility experiment contained grey, yellow, and white particles.   Since in a solubility series with products of this type, each solid will have assumed a different composition after a short time, and therefore any equilibrium which may have been set up between solid and solution will alter, a smooth solubility curve, and accurately reproducible results would not be expected.   Such considerations will account for the irregular results shown in Fig. 3.   The large decrease in the tungsten content of solution 17, after 687 days (v. Table IV) may be due to the decomposition of unstable higher tungstates, brought about by the above mentioned causes.

Solutions 20 and 30 were exceptional in that white hexagonal crystalline plates were deposited.   This crystallisation accounts for the fact that in the

[1] Loc. cit.
[2] Loc. cit.

final ultrafiltrates for 20 and 30, the tungsten contents are less than in 19 and 29, respectively, (Tables IV and V) whilst the pH value of 30 is much higher than for 28 and 29. (Table V).

(c)   Change in the particles of the disperse phase.   The remarks made under (b) apply in general to the particles of sols; ageing usually produces larger particles with less stability, and which therefore frequently coagulate.

(d)   Hydrolysis in the solutions may produce colloidal tungstic acid.   If the particles produced were small and heavily hydrated, clear sols may be produced.   This was the case in the following experiments: Type B, (Table IV, 18, 19, 20;) Type C, (Table VI, 21, 22, 23, 24).   In all these cases, the colloid content of the solution first increased, and then decreased with time; in some cases the value decreased to zero.   This effect is probably due to an increase in the size of the particles, accompanied by a change in the degree of hydration, followed by coagulation of the larger particles.   In some cases, presumably the whole of the colloidal tungstic acid was removed in this way.

In general, the changes in the amount of tungstic acid present in the colloidal state will be the resultant of the following effects: (a) dispersion of particles of the solid phase, (b) coagulation of aged particles in the sol.

Summary

Tungsten trioxide and four standard tungstic acids whose structures had been previously determined, have been subjected to the prolonged action of solutions of sodium hydroxide of varying concentration.   At stated intervals, the amount of tungsten in the solutions was determined before and after ultrafiltration through collodion membranes.   The pH values of certain solutions are recorded.   Changes in the solid phase have also been studied.   The results are discussed.

Municipal College of Technology,
University of Manchester,
June 15, 1931.

SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS. II

BY E. LESTER SMITH

In the previous paper of this series, attention was drawn to the extraordinary solvent powers of soap solutions for organic liquids insoluble or slightly soluble in water. The phenomenon was studied by determining the proportion of an organic liquid absorbed by a soap solution in equilibrium with excess of the liquid. In the present paper, the solvent properties of soap solutions will be studied from a different point of view. An organic substance almost insoluble in water—a sterol or an oil for example—may be dissolved to a limited extent in a soap solution; if this solution is then shaken with an organic solvent such as ether, the dissolved substance is by no means completely extracted by the solvent; on the contrary a definite and reproducible equilibrium is set up, the substance being partitioned between the two liquid phases.

Until recently almost the only problems involving the extraction of soap solutions occurred in connection with the analysis of oils, fats and waxes, where determinations of the quantity and nature of the unsaponifiable fraction afford in some instances criteria of genuineness. Very little systematic work is to be found in the literature, dealing with the problems underlying the extraction of soap solutions. Published papers include descriptions of analytical methods for the determination of the unsaponifiable matter in oils, fats and waxes, often unaccompanied by strict evidence as to their accuracy, and some experiments which prove that solvents such as petroleum spirit are less efficient than ethyl ether for the extraction of fish liver oil soap solutions. This work has been reviewed by the author elsewhere.[1]

With the discoveries that the fat-soluble vitamins A, D and E are present in the unsaponifiable fractions of the oils in which they occur, such studies assumed a new importance, particularly in connection with the preparation of concentrates of these vitamins for incorporation into foodstuffs and medicinal preparations. The work here reported was in fact undertaken initially from the point of view of these practical problems, but was continued on account of its own intrinsic interest. The unsaponifiable fraction of natural oils is a complex mixture of substances of ill-defined constitution, and is difficult to estimate with precision; the vitamins are even more difficult to estimate, and it was felt that more useful information might be obtained by studying instead the partition of some pure chemical substances.

p-Dimethylaminoazobenzene and aniline were finally selected, largely on account of the ease with which these basic substances could be extracted with acid from their solutions in organic solvents and estimated colorimetrically or volumetrically.

[1] Analyst, 53, 632 (1928).

Partition of p-Dimethylaminoazobenzene between Soap
Solutions and Ether

p-Dimethylaminoazobenzene is a yellow dye, almost insoluble in water, but fairly readily soluble in soap solutions and in organic solvents. Dilute solutions of its hydrochloride in hydrochloric acid have a pink colour, very suitable for colorimetric estimation. It was originally desired to study the partition of the natural unsaponifiable matter of cod-liver oil, and the idea was conceived of using this dye as an indicator, in the hope that it would be partitioned in the same ratio as the unsaponifiable matter. This hope received some justification in the fact that it had not proved possible (with rather crude analytical methods) to demonstrate any fractionation between the sterol and liquid portions of the unsaponifiable matter on successive extractions of a soap solution; nevertheless it was not fulfilled, as the dye showed a partition coefficient in favour of the ether phase considerably higher than the corresponding value for the unsaponifiable matter.

Previous experiments had indicated that the addition of methyl or ethyl alcohol increased the partition coefficient for unsaponifiable matter. Accordingly the effect of varying the methyl alcohol concentration on the partition of the dye was investigated, and also the effects of varying the soap concentration, the excess of alkali, and the concentration of the dye itself.

Experimental

The extractions were carried out in 250 cc stoppered separating funnels, into which all solutions were measured by pipette or burette, taking precautions against evaporation of ether. Fatty acids from cod-liver oil stearin were kept as a 50% stock solution in ether, which also contained the p-dimethylaminoazobenzene, in the proportion of 0.01 gm. to the fatty acids from 100 gm. of the oil. In most experiments the fatty acids from 15 gm. of oil were used, being mixed in the separator with the necessary amounts of water, 2 N sodium hydroxide, methyl alcohol and ether. After vigorous hand shaking for several minutes, the separators were allowed to stand at room temperature until complete separation into two layers occurred, noting the time required. The lower and upper layers were then run out separately into graduated flasks of capacity slightly greater than the volumes of the layers, afterwards filling to the mark with water-saturated ether measured from a burette. The volumes of the layers could thus be obtained by difference, with an error probably less than 0.5 cc. The ether layer was then transferred to a separating funnel, and extracted three times with 10% hydrochloric acid using 125 cc in all. The acid solution was warmed on a waterbath to remove ether, made up with water to 250 cc, and compared in a Hellige colorimeter with a standard containing 0.25 mg. of the dye in 100 cc of 5% hydrochloric acid. This gave the weight of dye in the ether layer, and from a knowledge of the total amount present, and the volumes of the layers, the partition coefficient could be calculated. The volume of ether used for an extraction was adjusted after some preliminary experiments, so that approximately half

the dye present was extracted since experimental errors in the estimation cause the least error in the calculation of partition coefficients under these conditions.

In the first series of experiments the fatty acids from 15 gm. of cod-liver oil stearin were made up to yield in every case a volume of 150 ccs of alcoholic soap solution (referred to as "10%" soap solution). On adding ether a very appreciable contraction occurred, and the final volume was always less than the sum of the volumes added by 5–10 cc, an amount considerably greater than could be accounted for by evaporation of ether during the measurements

Discussion of Results

Table I records the data for the first series of experiments in which the methyl alcohol concentration was varied, the concentrations of soap, alkali and dye remaining constant. The influence of methyl alcohol on the time required for complete separation of the emulsion is striking; 69 hours were needed in absence of the alcohol, only a quarter of an hour with 15% of methyl alcohol in the soap solution. The use of alcohols for breaking emulsions is of course a familiar procedure in analytical chemistry, but nevertheless it does not seem to be explained by any of the theories of emulsification that have been advanced.

In absence of methyl alcohol, the volume of the soap solution increases on saturation with ether from 150 cc to 187.5 cc. Additions of methyl alcohol up to about 25% cause only small increments in the ether absorption but higher concentrations of methyl alcohol greatly increase the absorption of ether by the alcoholic soap solution.

The partition coefficients after a very slight rise, decrease steadily with increasing methyl alcohol concentration; this point will be discussed later. Slight irregularities in these variations are due partly to experimental error and partly to variations in the room temperature at which the experiments were performed.

TABLE I

Initial Soap Concentration	Excess Na- OH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
10%	21.5%	Nil	69 hours	187.5 cc	37 cc	5.8
"	"	2%	?	189.5 cc	36.2 cc	5.8
"	"	5%	7 hours	188.3 cc	35.8 cc	6.0
"	"	10%	45 mins.	191.4 cc	33.2 cc	6.1
"	"	15%	15 "	190.7 cc	33.2 cc	5.6
"	"	20%	11 "	194.5 cc	30.0 cc	5.3
"	"	25%	10 "	199.9 cc	23.8 cc	4.5
"	"	27%	5 "	200.4 cc	43.0 cc	4.2
"	"	33%	5 "	219.0 cc	29.2 cc	3.0
"	"	40%	3.5 "	250.0 cc	57.5 cc	2.15

TABLE II

Initial Soap Concentration	Excess NaOH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time to Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
10%	1%	20%	?	193.0 cc	30.3 cc	5.4
"	21.5%	"	11 mins.	194.5 cc	30.0 cc	5.3
"	42%	"	18 "	198.5 cc	25.0 cc	4.55
"	1%	33%	5 "	212.5 cc	39.7 cc	3.55
"	21.5%	"	5 "	219.0 cc	29.2 cc	3.0

TABLE III

Initial Soap Concentration	Excess NaOH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time to Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
8%	21.5%	20%	7 mins.	184.2 cc	36.0 cc	7.85
10%	"	"	11 "	194.5 cc	30.0 cc	5.3
12%	"	"	6 "	205.5 cc	41.5 cc	3.95
14%	"	"	8 "	221.5 cc	34.8 cc	3.55
16%	"	"	7 "	236.0 cc	48.0 cc	2.9

The second table indicates that for a fixed soap concentration of 10% and methyl alcohol concentration of 20% and 33%, respectively, increasing the free alkali in the soap solution slightly increases the ether absorption and decreases the partition coefficient.

The third table illustrates the effect of increasing soap concentration for a fixed methyl alcohol concentration of 20%. The ether absorption is observed to increase rapidly, while the partition coefficient falls from 7.85 to 2.9 on doubling the soap concentration.

Interpretation of Results

We have seen in the first paper of this series, that the solvent powers of soap solutions can only be accounted for by postulating adsorption of the organic solute on the colloidal soap particles. The resistance which such solutions show towards extraction of the solute by organic solvents favours the same hypothesis. Fortunately also, some of the partition data are amenable to mathematical treatment which enables the hypothesis to be tested.

It is convenient to consider the solute as being distributed between three phases, the organic solvent, the water and the colloidally dispersed soap. The portions of solute in the solvent and in the water, respectively, are in equilibrium according to the law of partition, while the portions of solute in the water and in the soap micelles are in equilibrium according to the adsorption law. It is true that the concentration of solute in the water may be vanishingly

small in some cases, and also that solute may pass direct from soap to solvent, but these considerations do not render inapplicable the above equilibrium relationships.

Thus we have:—

Let U = Total weight of solute in system.

X = Weight of solute adsorbed by colloidal soap.

Y = Weight of solute in true solution in aqueous phase (excluding that adsorbed by the soap).

W = Weight of solute in organic solvent phase.

k_1 = Adsorption coefficient.

k_2 = True partition coefficient for solute between organic phase and aqueous phase (without colloidal soap).

K = Measured partition coefficient for solute between organic phase and aqueous plus colloidal soap phases.

v = Volume of organic solvent phase.

V = Volume of aqueous phase.

S = Concentration of colloidal soap in aqueous phase.

Then according to the usual adsorption formula:—

$$(1) \qquad X = k_1 \, S \, Y^{1/n}$$

$$(2) \qquad \text{or } Y = \frac{X^n}{k_1{}^n \, S^n}$$

According to the partition formula:—

$$(3) \qquad \frac{W}{Y} = \frac{k_2 v}{V}$$

Substituting for Y,

$$(4) \qquad \frac{W}{X^n} = \frac{k_2 v}{k_1{}^n S^n V}$$

$$(5) \qquad U = X + V + W$$

But since Y is usually extremely small, it can be neglected in comparison with U giving:—

$$(6) \qquad X = U - W$$

Substituting in (4),

$$(7) \qquad \frac{W}{(U-W)^n} = \frac{k_2 v}{k_1{}^n S^n V}$$

The ordinary partition formula used for calculating K (in which aqueous and colloidal phases are treated as one phase) is:—

$$(8) \qquad \frac{W}{(U-W)} = \frac{K v}{V}$$

Whence:—

$$(9) \qquad K = \frac{k_2}{k_1{}^n S^n} (U-W)^{n-1}$$

If this expression is correct we should expect that the measured partition coefficient K would not remain constant if the amount of solute in the aqueous layer varied over any considerable limits.

It would only remain constant if n = 1, when the expression $(U-w)^{n-1}$ reduces to 1. This would be the case if the solute distributed itself between the colloidal soap and the aqueous phases according to the simple law of partition and not according to the usual adsorption law. In a series of experiments, however, it may be taken that small variations in the concentration of solute in the aqueous phase will not affect the value of K, the permissible limits of variation becoming smaller the further the value of n departs from 1.

We should also expect that K would be increased by any factor which would increase the true partition coefficient k_2 and decreased by any factor tending to increase either the adsorption coefficient or the concentration of colloidal soap (not total soap concentration) in the aqueous layer.

Tables I-III provide data which enable some of these conclusions to be tested. Table III shows the pronounced influence of soap concentration of the partition coefficient K; the value of the latter is reduced to much less than half its former value by doubling the soap concentration. This is in agreement with expectations, since according to formula (9) K should be proportional to $1/S^n$; S, the concentration of colloidal soap, would more than double on doubling the total soap concentration, since a relatively greater proportion would be in molecular solution in the weaker solution; also n is greater than 1; both these factors therefore tend to make K decrease more rapidly than the soap concentration increases.

Similarly the effect of excess alkali in the alcoholic soap solution would probably be to increase the proportion of soap in the colloidal state, without much affecting other factors. This is reflected (see Table II) in an increase in the ether absorbed by the soap solution, and a decrease in the partition coefficient K.

Variation in the methyl alcohol concentration has a composite effect. On the one hand, the solubility of the solute in the aqueous phase is likely to increase with increasing alcohol concentration, and since its solubility in the organic phase is not much affected, k_2 the ratio of these solubilities, decreases, so that K tends to decrease. On the other hand, the soap passes more completely into molecular solution as the alcohol concentration is increased, so that S decreases; also the increased solubility of the solute in the aqueous phase is liable to decrease the adsorption coefficient k_1. Both these factors tend to increase K so that the net effect on K cannot be predicted.

Table I shows in the main a decrease in K for increasing methyl alcohol concentration, indicating, if formula (9) is correct, that k_2 decreases more rapidly than $k_1^n S^n$. Neither of these factors can be measured with any degree of accuracy under the conditions of the experiments; it was possible, however, to get a rough measure of k_2 by making the assumption that the solubility of the solute in the aqueous phase (containing methyl alcohol, dissolved ether, and soap in molecular solution) is the same as its solubility in aqueous methyl alcohol of the same strength.

The solubility of the dye in a series of methyl alcohol-water mixtures was therefore determined, by adding the requisite volume of a methyl alcohol solution of the dye to a measured volume of water, allowing the excess dye to crystallise out overnight, and estimating colorimetrically the dye concentration in the acidified filtrate. The solubility of the dye in ether at $15.5°$ was found to be 2.99 gm. per 100 cc of solution. The ratio of the solubilities in ether and in aqueous methyl alcohol gives k_2 approximately. Since $(U-W)^{n-1}$ was approximately constant for the experiments recorded in Table I, $k_1{}^n S^n$ is proportional to K/k_2. The results obtained are shown in Table IV, a few of the intermediate values for k_2 being read from curves. It will be observed that the solubility of the dye in water increases rapidly with increasing methyl alcohol concentration, so that k_2 decreases in like fashion. The values of k_2/K in the last column, which should be proportional of $k_1{}^n S^n$, also decrease, though less rapidly than does k_2, thus confirming the previous conclusion. In other words, the addition of methyl alcohol has a greater effect in increasing the solubility of the dye in the aqueous phase than it has in decreasing the proportion of soap in the colloidal state and the value of k_1; hence the measured partition coefficient K falls.

TABLE IV

Methyl Alcohol as % of initial volume of soap solution	Solubility of Dye (parts per 10^6)	K_2	K	$k_2/K \propto k_1{}^n S^n$
0%	0.32	93,000	5.8	16,000
5%	0.41	73,000	6.0	12,000
10%	—	43,000	6.1	7,100
15%	1.00	30,000	5.6	5,400
20%	1.95	15,000	5.3	2,900
25%	—	11,900	4.5	2,700
27%	—	10,300	4.2	2,500
30%	3.35	—	—	—
33%	—	6,400	3.0	2,100
40%	10.2	2,900	2.15	1,300

Determination of "n"

A further series of experiments was planned to determine partition coefficients for widely differing concentrations of the dye. This provides data for the calculation of a series of values for the index "n," the constancy of which afford a further test of the validity of formula (9). If all factors except solute concentrations are kept the same in two experiments (for which the subscripts a and b are used) we have:

$$(10) \quad \frac{K_a}{K_b} = \frac{(U-W)_a^{n-1}}{(U-W)_b^{n-1}}$$

$$(11) \quad n = \frac{\log \dfrac{K_a}{K_b}}{\log \dfrac{(U-W)_a}{(U-W)_b}} + 1$$

Partition coefficients were measured for the dye p-dimethylaminoazobenzene using a 20% concentration of methyl alcohol, and other concentrations as in the first series of experiments, except that the fatty acids were prepared from cod-liver oil stearin soap solution exhaustively extracted with ether to remove unsaponifiable matter, in case this might interfere. The temperature at which the separations occurred was maintained at $19° \pm 1°$.

<div align="center">TABLE V</div>

Initial Weight of Dye	K	(U − W)	n
1.0 gm.	6.55	0.574 gm.	
			1.063
0.10 ″	5.72	0.0663 ″	
			1.065
0.010 ″	4.86	0.00563 ″	
			1.069
0.0010 ″	4.18	0.00063 ″	
			1.070
0.00010 ″	3.60	0.000072 ″	

The results, recorded in Table V, show that the value of n remains constant within the limits of experimental error. Owing to the fact that n is only slightly greater than 1, the partition coefficient is barely doubled for a 10,000 fold increase in initial dye concentration. This means that it would almost be correct to say that the dye is dissolved, rather than adsorbed, by the colloidal soap, a conclusion which is of interest in connection with the further experiments to be described.

<div align="center">

Partition of Aniline between Sodium Oleate Solutions and Ethyl Acetate

</div>

The experiments described in this section were carried out three years later than those in the preceding section, and in connection with an investigation of the system sodium oleate, water, sodium chloride, ethyl acetate, which will form the subject of a later communication.

Sodium oleate was chosen as a pure soap, of which isotropic solutions could be prepared over a considerable concentration range at room temperature; ethyl acetate because it was one of the few organic solvents known at the date of these experiments which did not form a permanent emulsion when shaken with a soap solution; aniline because it could easily be estimated volumetrically and because it was more soluble in water than other solutes investigated and promised to yield interesting results on this account.

Experimental. Sodium oleate was prepared as described previously. Ethyl acetate was purified by washing repeatedly with calcium chloride solution or brine to remove alcohol, drying over calcium chloride and fractionating. Aniline of C.P. quality was freshly redistilled before use.

To determine a partition coefficient, sodium oleate solution and a solution of aniline in ethyl acetate were weighed into a 100 cc separating funnel, which was stoppered both at the top, and at the bottom of the stem, and then

immersed to the neck in a thermostat at 25°. After a period sufficient to ensure temperature equilibrium, the separator was shaken vigorously by hand, and replaced in the thermostat until separation was complete. It was then carefully removed and samples comprising almost the whole of each layer transferred to weighed separating funnels. The aniline was estimated in both samples, so that the concentration of aniline per gram could be calculated for both layers, the ratio of these concentrations being taken as the partition coefficient. This method of calculating partition coefficients needs no apology, for as Hand remarks[1] Nernst's original statement of the partition law was in terms of weight in weight concentrations. Aniline was extracted from the ethyl acetate layer by shaking out thrice, each time with a quantity of 10% sulphuric acid approximately equal in volume to the sample. The bulked acid extracts were boiled down to small bulk to remove ethyl acetate and alcohol resulting from its hydrolysis (acetic acid was found not to affect the estimation) cooled and transferred to a stoppered bottle with enough water to bring the acidity back to about 10% sulphuric acid. Aniline was then estimated volumetrically in this solution by the method of Pamfilov and Kisseleva[2]. About 1 gm. of potassium bromide was added, then a measured excess of $N/10$ sodium hypobromite solution (usually 50 cc); after standing about 3 minutes, 1 gm. of potassium iodide was added in solution, and the mixture back-titrated with $N/10$ sodium thiosulphate using starch as indicator. Aniline was extracted similarly from the soap solution after adding a little more ethyl acetate, but it was necessary to filter the acid solution before titrating, in order to remove the trace of oleic acid usually present, which was found to interfere with the aniline estimation. Tested against pure aniline this volumetric method gave results 1-2% too high. No corrections were applied however since the same errors affected the estimations of aniline in both phases, and cancelled out in the calculation of the partition coefficient.

Partition coefficients for aniline were measured over the largest possible range of sodium oleate concentrations, namely from zero to 1.1 N_w. Slightly above the latter concentration a third liquid phase appeared, which was characterised as neat soap on account of its properties, and from a knowledge of the phase diagram which will be described in the next paper in this series. In some experiments the aniline concentration was varied over as wide a range as was practicable, and in others the effect of sodium chloride on the partition coefficient was studied.

The initial sodium oleate concentrations are expressed in weight normalities (mols of soap associated with 1 kilo of water) and also as weight in weight percentages. The weight normality is not affected by saturation with ethyl acetate, and shaking with excess ethyl acetate alters it only very slightly on account of the water abstracted from the soap solution by the upper layer.

Discussion of Results

The results are combined in Table VI. Owing to the moderate solubility of aniline in water, the partition coefficient for this substance between ethyl

[1] J. Phys. Chem., **34**, 1961 (1930).
[2] Z. anal. Chem., **75**, 87 (1928); Analyst, **54**, 60 (1929).

TABLE VI

Initial Sodium Oleate		Initial Sodium Chloride N_w	Aniline. Gm. per 100 gm. Solution		Partition co-efficient $K = \dfrac{(A)_1}{(A)_2}$
N_w	Gm. per 100 gm. solution		$(A)_1$ Upper Layer	$(A)_2$ Lower Layer	
o	o	—	0.442	0.0146	30.2 ⎱ Mean 30.25
,,	,,	—	0.550	0.0182	30.3 ⎰
,,	,,	—	0.0561	0.00182	30.7
,,	,,	—	4.62	0.157	29.5
,,	,,	0.5	0.481	0.0146	33.0
0.05	1.50	—	0.542	0.0242	22.4
0.1	2.95	—	0.539	0.0320	16.8
0.1	2.95 .	0.5	0.399	0.0256	15.6
0.15	4.37	—	0.436	0.0360	12.1
0.2	5.73	—	0.316	0.0303	10.5
0.3	8.36	—	0.396	0.0502	7.9
0.4	10.83	—	0.517	0.0728	7.1 ⎱ Mean 7.05
0.4	10.83	—	0.528	0.0752	7.0 ⎰
0.4	10.83	—	3.82	0.534	7.15
0.4	10.83	—	16.90	2.239	7.55
0.4	10.83	0.5	0.422	0.0610	6.9 ⎱ Mean 6.85
0.4	10.83	0.5	0.439	0.0648	6.8 ⎰
0.5	13.2	—	0.501	0.0844	5.93
0.7	17.55	—	0.509	0.1106	4.61
0.9	21.5	—	0.649	0.1584	4.10 ⎱ Mean 4.10
0.9	21.5	—	0.620	0.1507	4.11 ⎰
1.1	26.7	—	0.469	0.1229	3.82

acetate and water is not abnormally high, like the corresponding value for p-dimethylaminoazobenzene between ether and water.

It will be observed however that 1% of sodium oleate is sufficient to cause a marked decrease in the partition coefficient for aniline, and that the value decreases steadily as the soap concentration increases. Comparison with Table III will show that this decrease in K is of lesser magnitude than in the earlier experiments using the dye as solute. This is largely because the amount of aniline dissolved in the water phase is comparable with the amount dissolved in the colloidal soap phase, a factor which operates in the direction of making K independent of soap concentration. It was hoped that these statements might be expressed mathematically, but although a formula can be derived along the lines of the one used in connection with the earlier experiments, the fact that Y cannot be neglected in comparison with U and X renders the final expression so complicated that it cannot be made to yield any useful information. It will be observed that K is independent of aniline concentration, except when this is so high that the weight of aniline adsorbed by the soap is comparable with that of the ethyl acetate adsorbed. This means that the value of n in the adsorption formula is unity, so that in this case it is hardly correct to speak of adsorption of solute by the soap. Rather

must the aniline be regarded as being distributed according to the partition law between the three phases; (1) wet ethyl acetate layer; (2) water (plus dissolved ethyl acetate and soap in molecular solution); and (3) colloidal soap (plus adsorbed ethyl acetate and water of hydration).

The effect of sodium chloride is noteworthy. It *increases*, by the familiar salting-out effect, the partition coefficient for aniline between ethyl acetate and water. When soap is present, however, salt *decreases* the partition coefficient below the corresponding value in the absence of salt. This is attributed to the effect of salt in increasing the proportion of the soap in the colloidal state, thus increasing the size of this phase in relation to the others.

It may be noted in passing that the temporary emulsion produced by shaking 0.9 N_w sodium oleate solution with ethyl acetate is perfectly transparent at 25°.

In general, this series of experiments using aniline as solute confirm the conclusion suggested by the earlier experiments. Both series demonstrate clearly the remarkable solvent powers of colloidal soap. Consideration of the magnitudes of the partition coefficients in conjunction with those of the corresponding soap concentrations indicates that the solubilities of the dye or the aniline in the colloidal soap phase must be comparable with their solubilities in organic solvents. This solvent power of soap is even more in evidence when the solute is the natural unsaponifiable matter of oils, for the available data indicate partition coefficient of ½ to ⅓ the corresponding values for the dye or the aniline.

Partition between Water and Colloidal Soap

When the organic solvent phase is absent, and a small proportion of a solute such as aniline is added to a soap solution, the solute must be distributed between the remaining two phases, water and colloidal soap. Such partition or adsorption phenomena can only be studied indirectly, but two examples of their effects may be cited from the literature. McBain and Bolam[1] and Beedle and Bolam[2] measured the hydrolysis alkalinity of soap solutions by the catalytic effect of the hydroxyl ion on the decomposition of nitrosotriacetonamine. They obtained abnormally low results for the more concentrated soap solutions and ascribed the discrepancy between determinations by this and by electrical methods to adsorption of the amine on the soap micelles. Hampil[3] found that soap had a marked inhibiting effect on the germicidal activity of phenolic compounds towards *B. Typhosus* and other organisms; thus 0.5% of sodium oleate destroyed the activity of hexyl resorcinol at a dilution of 1:1000 which is at least five times the strength necessary to kill the organisms in the same time in aqueous solution. Hampil considered the distribution of the phenolic substance between the water and the colloidal soap, as the most probable explanation of these phenomena.

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[1] J. Chem. Soc., **113**, 825 (1918).

[2] J. Soc. Chem. Ind., **40**, 27T (1921).

[3] J. Bact., **16**, 287 (1928).

The Extraction of Soap Solutions

We may now consider the bearing of these conclusions on the original problem of how best to extract organic substances dissolved in soap solutions. The first desideratum is evidently that the soap should be as far as possible in true or molecular solution, with the minimum proportion present as colloid. This may be achieved by the use of solvents which tend to render the soap "less colloidal," such solvents being in general those which are appreciably soluble in water, as shown in the first paper of this series.[1]

The same result may be secured by the addition of alcohols. The measurements with p-dimethylaminoazobenzene show, however, that this beneficial effect of alcohol may be counterbalanced by its effect in increasing the solubility of the solute in the aqueous phase. The choice of a solvent of the type suggested, or the use of alcohol, has a second very practical advantage in that the emulsions produced by shaking are relatively impermanent. The value of the adsorption coefficient for the solute by the colloidal soap is usually outside our control. The partition coefficient on the other hand, is evidently proportional to the solubility of the solute in the extracting solvent, if other factors remain unchanged.

In connection with the extraction of unsaponifiable matter from fish liver oil soap, it was sought to utilise this principle by determining the solubility of cholesterol, which constitutes a considerable proportion of the unsaponifiable matter, in a series of solvents. The solubilities decreased in the order ether, benzene, petroleum spirit; the partition coefficients for the same soap concentration decreased in the same order, but not proportionately, because other factors did not remain constant. In practice, the choice of solvents is limited chiefly by the tendency of most solvents to emulsify in the soap solution, and the large proportion of alcohol necessary to break the emulsions so produced. Such solvents as benzene and its homologues, chloroform and chlorinated hydrocarbons generally are unsuitable on this account except in special cases.[2] When mixed with sufficient alcohol to render emulsions unstable, the proportion of solvent absorbed by the soap solution becomes unduly high. Also in some cases (noted particularly in the extraction of unsaponifiable matter with xylene from alcoholic soap solution), the value of n (see formula 9) is large, so that the efficiency of extraction decreases rapidly as the weight of solute remaining behind in the soap solution is reduced. Petroleum spirit does not suffer from these defects, even when the proportion of alcohol in the soap solution is over 50%, but the partition coefficients for unsaponifiable matter are too low to render this solvent serviceable in this connection.[3] Ether is the most generally useful solvent for extracting soap solutions, requiring relatively little alcohol to break its emulsions. Ethyl acetate, however, deserves attention as it does not emulsify even in absence of alcohol and is a good solvent for many organic substances. Its disadvantages are that the soap solution must be neutral in order to avoid

[1] J. Phys. Chem., **36**, 1401 (1932).

[2] See for example Smith and Hazley: Biochem. J., **24**, 1942 (1930).

[3] See Smith: Analyst, **53**, 632 (1928).

hydrolysis of the ester, and that more fatty acid is extracted from a neutral than from a slightly alkaline soap solution.

The extraction of soap solutions is no exception to the general rule that the efficiency of extraction increases as a given total volume of extracting solvent is subdivided into smaller portions. In practice however, both in laboratory extractions for the determination of unsaponifiable matter, and in large-scale extractions for the preparation of fat soluble vitamin concentrates, it is found best to give only 3 or 4 extractions. For a given degree of extraction, the solvent saved by giving more extractions with a smaller total volume is more than counterbalanced by the extra time consumed in the operations. The author has shown elsewhere that in general the greatest efficiency is secured by subdivision of the extracting solvent into *equal* portions.[1] The rule applies to the extraction of soap solutions when the value of "n" approximates to unity. When "n" is greater than 1, it can be shown mathematically that it is more efficient to extract with decreasing volumes of solvent.

Summary

Partition coefficients have been measured for the dye p-dimethylamino-azobenzene between ether and soap solution.

The partition coefficients decrease considerably with increasing soap concentration, and slightly with increasing methyl alcohol concentration, and with increasing excess alkali, in the soap solution.

The results are explained by postulating adsorption of the dye on the colloidal soap.

A formula has been derived on the assumptions that the solute is distributed between the colloidal soap and the aqueous phases according to the adsorption law, and between the organic solvent phase and the water according to the partition law.

The formula receives quantitative confirmation in the decrease of the partition coefficients with decrease in the dye concentration.

The addition of methyl alcohol greatly increases the solubility of the dye in the aqueous phase and so decreases the partition coefficients, despite the counterbalancing effect of the alcohol in diminishing the proportion of soap in the colloidal form.

Partition coefficients have also been measured for aniline between ethyl acetate and sodium oleate solutions.

The partition coefficients decrease considerably with increasing soap concentration and decrease slightly on addition of sodium chloride, but are almost independent of aniline concentration.

The system behaves as though the aniline were distributed according to the partition law between the three phases, ethyl acetate, water, and colloidal soap.

The bearing of these experiments on the problem of how best to extract organic solutes, particularly the natural unsaponifiable matter of oils and the attendant fat-soluble vitamins, from soap solutions, is discussed.

Glaxo Research Laboratory, London, N. W. 1.
Research Laboratory, Chelsea Polytechnic, London, S. W. 3.
January 12, 1932.

[1] J. Soc. Chem. Ind., **47**, 159T (1928).

THE ACTIVITY COEFFICIENT OF BENZOIC ACID IN SOLUTIONS OF NEUTRAL SALTS AND OF SODIUM BENZOATE*

BY I. M. KOLTHOFF AND WOUTER BOSCH[1]

In previous papers, the authors[2] have studied the influence of neutral salts on the activity coefficients of the anions of weak acids. The hydrogen ion activity of a very dilute buffer mixture of a weak acid and its salt, to which known amounts of neutral salts had been added, was measured and from these data the activity coefficients of the anion of the acid computéd. In working with systems containing an undissociated acid and its monovalent anion, the difficulty was encountered that the change of the activity coefficient of the undissociated acid in the presence of neutral salts was not exactly known.[2] For this reason, it was decided to make a more extensive study of the system, benzoic acid-sodium benzoate, in which the activity coefficient of the undissociated acid could be kept constant or be determined in an experimental way.

In the second paper the results of the measurements of the activity coefficient of the benzoate ion in the system benzoic acid (saturated solution in water), o.o1 N sodium benzoate in the presence of various concentrations of neutral salts will be described.

In the third paper of this series the activity coefficient of the silver ions in a saturated solution of silver benzoate in the presence of various concentrations of the same neutral salts will be reported. From the silver ion activity and the solubility product of silver benzoate the activity coefficient of the benzoate ion could be computed and the figures compared with those found in the second paper in solutions of nearly the same ionic strength.

Materials used

Water: Conductivity water was used throughout this work.

Benzoic acid: A U.S.P. product (Eastman Kodak Company) was recrystallized a few times by pouring a concentrated solution in hot alcohol into a large volume of boiling water. After cooling, the crystals were collected by suction and dried over sulfuric acid to constant weight. Various tests (for details see thesis of W. Bosch) showed that the product was chemically pure. In addi-

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tion the normality of a solution of sodium hydroxide was determined according to standard methods with our product, one of the Bureau of Standards and one of Kahlbaum (für kalorimetrische Bestimmungen); all data agreed within 0.02%. In order to test the physical purity (possible presence of another modification) various amounts of solid body (between 0.8 and 6 g. with 200 cc. water) were used in solubility measurements; in all cases the data obtained agreed within 0.1%. If the saturated solution was poured off from the solid body and fresh water added, the same solubility was found. Moreover, Kahlbaum's product, before and after melting, gave exactly the same results as our own product.

Sodium benzoate: A U.S.P. product (Merck) was twice recrystallized from water, washed with small amounts of cold water, finally with a small volume of absolute alcohol, and dried at 150° to constant weight. By qualitative and quantitative tests its purity was established. Moreover, in many of the experiments, solutions of sodium benzoate were prepared from pure benzoic acid and standard base; exactly the same results were obtained as with solutions of the above salt of equivalent concentration.

Neutral salts: C. P. salts were used, some of them recrystallized from water and their purity tested according to standard methods. Very sensitive tests were applied to establish the absence of acidic or basic impurities, (for complete description, comp. thesis of W. Bosch, p. 26-32) moreover, the water content of hydrates was determined in a quantitative way. It may be mentioned that the strontium nitrate was labelled as being a hydrate, whereas it did not contain more than 0.25% water.

Solubility of Benzoic Acid in Water and in Sodium Benzoate

The solubility was determined in a thermostat at 25° ± 0.01°. Weighed samples of benzoic acid with 200 cc. of water or salt solution were rotated in Pyrex glass bottles, closed with paraffined cork stoppers. After saturation had been reached, the bottles were allowed to stand in the thermostat until the supernatant liquid was clear and samples drawn out with the aid of suction with a carefully calibrated pipet at 25°. The tip of the pipet was connected with a piece of glass tubing, the latter being drawn out in the middle and filled with adsorbent cotton. The clear solution was titrated with standard carbonate-free sodium hydroxide, using phenolphthalein as an indicator. As a rule 1.5 g. benzoic acid was used in a volume of 200 cc.; the amount of acid, however, proved to be immaterial. In agreement with M. Kilpatrick Jr. and E. F. Chase,[3] it was found that after five hours' shaking the solution was saturated; as a rule, however, the bottles were rotated over night.

All concentrations are expressed in moles per liter. As an average of thirty determinations with different amounts and products of benzoic acid a solubility of 0.02775 ± 0.00002 moles acid per liter at 25° was found, this

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[3] M. Kilpatrick Jr. and E. F. Chase: J. Am. Chem. Soc., **53**, 1732 (1931).

figure being in close agreement with the data reported in the literature (compare list given byKilpatrick and Chase[3]).

The activity of the undissociated acid is smaller than the saturation value, since a small part of the acid is dissociated into its ions.

$$[aH \; Benz] = 0.02775 - cH^+$$

in which cH^+ represents the hydrogen ion concentration (not the activity) of the saturated solution in water. As will be shown later, the ionization constant of benzoic acid at $25°$ is equal to 6.60×10^{-5}. From this and the saturation figure, it is found that the hydrogen ion activity in the saturated solution is equal to 1.31×10^{-3}. By applying the simple Debye-Hückel relation:

$$- \log f = 0.5 \sqrt{\mu}$$

a hydrogen ion concentration of 1.36×10^{-3} is calculated and the activity of undissociated benzoic acid in the saturated solution in water is found to be $0.02775 - 0.00136 = 0.0264$.

Since this calculation involves the use of some slightly uncertain data, the activity of the undissociated acid was also derived in another way. The solubility of benzoic acid was determined in solutions of sodium benzoate of varying concentrations and the data after correction for the dissociated part plotted in a curve. By extrapolation to a sodium benzoate concentration equal to zero the activity of the acid is found. The correction for the dissociated part of benzoic acid in sodium benzoate is extremely small, as the common ion depresses the ionization of the acid. For example, in 0.01 N sodium benzoate, a solubility of benzoic acid of 0.02670 moles per liter was found, whereas the hydrogen ion activity as determined with the hydrogen electrode was found to be equal to 2.15×10^{-4}, or the hydrogen ion concentration approximately 2.4×10^{-4}. Therefore, the concentration of undissociated acid in 0.01 N sodium benzoate is $0.02670 - 0.00024 = 0.02646$. The correction for the dissociated part decreases with increasing benzoate concentration, which is rather fortunate, as the activity coefficient of the hydrogen ions is not kno$\overset{.}{\text{w}}$n and the accurate measurement of the hydrogen ion activity in such solutions is extremely hard.

A summary of the results is given in Table I. Sol. benz. acid denotes the experimental value of the solubility of benzoic acid in moles per liter, (cHB) the concentration of the undissociated acid, f_o the activity coefficient of the undissociated acid in the benzoate solutions.

$$f_o = \frac{[cHB]_o}{[cHB]_{Benz}}$$

$(cHB)_o$ is the extrapolated value of the concentration of the undissociated acid at a sodium benzoate concentration equal to zero, whereas $(cHB)_{Benz}$ denotes the same in the benzoate solution of indicated strength.

<div align="center">TABLE I</div>

<div align="center">Solubility of Benzoic Acid in Sodium Benzoate and Inner Complex Constant
at 25°</div>

Sodium benzoate m. per l.	Sol. benz. acid moles per liter	$[aH^+]$	$[cHB]$	f_0	$[cHB_2^-]$	K
1.00	0.04623		0.04623	0.570	0.01988	1.3
0.75	.03933		0.03933	.671	.0298	1.5
0.5	.03398		.03398	.778	.00763	1.7
0.25	.02934	1.22×10^{-5}	.02933	.989	.00299	2.2
0.1	.02757	2.44×10^{-5}	.02754	.958	.00122	2.1
0.05	.02704	4.57×10^{-5}	.02699	.976	.00069	1.9
0.03	.02682	7.31×10^{-5}	.02674	.985	.00047	1.6
0.02	.02672	1.1×10^{-4}	.02660	.992		
(0.01	.02670	2.15×10^{-4}	.02648	.997)		
0.00			.02635	1.000		

The extrapolated value of the activity of the undissociated acid at an ionic strength of zero corresponds to a concentration of 0.02635, in close agreement with the value of 0.0264 calculated from the solubility of the acid in pure water and that of 0.0265 computed by Kilpatrick and Chase[3] at 25.15°.

As may be seen from the figures in Table I, f_0 decreases with increasing sodium benzoate concentrations, a fact already found by E. Larsson.[4] As a rule the activity coefficient of a non-electrolyte increases with increasing ionic strength (salting-out effect); from other measurements (vide infra), it is evident that sodium ions exert such a salting out effect; therefore, the decrease observed with sodium benzoate has to be attributed to a specific interaction between the benzoate ion and benzoic acid. Larsson[4b] thinks it possible that we are dealing here with the formation of acid benzoate ions, as acid benzoates may crystallize from solutions, saturated with benzoic acid. "Jedoch musz man sehr vorsichtig sein aus der Bildung solcher Verbindungen auf ihre Existenz in Lösung zu schliessen. Hierin können sie vollständig dissoziiert sein." According to the authors' opinion, there seems to be little doubt that the benzoate forms a kind of inner complex with benzoic acid. It is known that benzoic acid in more concentrated solutions has a tendency to associate to give double molecules. This association is facilitated by the formation of the anion of the double molecule:

$$HB + B^- \leftrightarrows HB_2^-$$
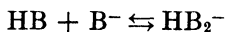
the case being somewhat similar to the inner complex formation of boric acid. If the above equation gives a true picture of what is happening, the following expression should hold:

$$[aHB] \cdot \frac{[aB^-]}{[aHB_2^-]} = K$$

Since B− and HB₂− both represent anions of a similar type, it can be approximately written:

$$[aHB] \frac{[cB^-]}{[cHB_2^-]} = K$$

[4] E. Larsson: Z. physik. Chem., (a) **148**, 148 (1930); (b) **153**, 466 (1931).

The experimental test of this equation meets with some difficulties. [aHB] is equal to 0.02635 at 25° since all solutions were saturated with respect to benzoic acid. It is harder to find the concentration of the associated anion HB_2^-. At first sight, it seems that $[cHB_2^-]$ is equal to the total concentration of the undissociated acid in the benzoate solution ([cHB] in Table I) minus the activity of the benzoic acid (0.02635). This, however, is not true for two reasons: Part of the HB_2^- ions will combine with hydrogen ions to form associated molecules of benzoic acid $(HB)_2$. Since the concentration of the later is negligibly small in a saturated solution of benzoic acid in water at 25°, it is assumed here that its concentration is equally negligible in the benzoate solutions which would mean that the associated benzoic acid behaves as a much stronger acid than the single molecules. A similar relation is found again with boric acid.

The values of $[cHB_2^-]$ in Table I have been calculated on the assumption that the associated acid is entirely present in the anion form. Even if this assumption holds rigorously an absolute constant value of K cannot be expected as the salting-out effect is neglected. It is quite certain that sodium ions decrease the solubility of benzoic acid, whereas it may be expected that the benzoate ions also exert such a salting-out effect which in the present case is masked by the complex formation. Since the salting-out effect is not a linear function of the ionic strength ($-$ log f_o is a straight line function of μ) a deviation from constant values can be expected at increasing sodium benzoate concentrations. Moreover, it should be added that if instead of sodium benzoate another alkali benzoate had been used, say potassium, a different value for K would have been found since the salting-out effect of potassium is less than that of sodium.

The values of K in Table I have been calculated on the assumption that $[cHB_2^-] = [cHB] - 0.02635$, and $[cB^-] = [cNa \text{ benzoate}] - [cHB_2^-]$. In a similar way the value of K has been calculated at 18° from data of E. Larsson.[4a]

TABLE II

Solubility of Benzoic Acid in Sodium Benzoate and Inner Complex Constant at 18° (Larsson)

Sodium benzoate moles per liter	[cHB]	f_o	$[cHB_2^-]$	K
1.000	0.0351	0.61	0.0135	2.05
0.930	0.0341	.628	0.0125	2.22
0.698	0.02946	.724	0.00786	2.08
0.500	0.0268	.800	0.0052	2.06
0.465	0.02638	.813	0.00478	1.90
0.2325	0.02383	.900	0.00223	1.59
0.1032	0.02265	.947	0.00105	1.58
0.000	0.02160	1.00		

Although no strict constant value for K is found, which theoretically is not to be expected, there seems to be little doubt that the increase of the solubility of benzoic acid in sodium benzoate must be attributed to the formation of

anions of the associated benzoic acid molecules. Comparing the values by Larsson at 18° (Table II) with those in Table I reveals that the complex ions become less stable at higher temperatures, a behavior similar again to that of the inner complexes of boric acid.

The Activity of Benzoic Acid in Neutral Salt Solutions

The solubility of benzoic acid was determined in 0.01 N sodium benzoate as a solvent in the presence of various amounts of neutral salts. As before concentrations are expressed in moles per liter. The results are given in Table III. f_o has been calculated by dividing the solubility of the acid in 0.01 N sodium benzoate by that found in the presence of neutral salts. A correction for the dissociated part of the acid does not have to be considered, as it is about the same in all solutions and very small as the ionization of the acid is suppressed by the excess of benzoate.

TABLE III

Activity Coefficient f_o of Benzoic Acid in Salt Solutions in the Presence of 0.01 Molar Sodium Benzoate at 25°

Salt added to 0.01 molar Na benzoate	Ionic strength salt	Normality salt	Normality benzoic acid	f_o	$+ \log f_o$
—	0.01	0.01	0.02676	1.000	.000
KCl	.09	.09	.02588	1.033	.0142
,,	.25	.25	.02456	1.089	.0370
,,	.50	.50	.02266	1.180	.0718
,,	1.00	1.00	.01938	1.380	.1398
NaCl	.09	.09	.02568	1.042	.0179
,,	.25	.25	.02408	1.111	.0457
,,	.50	.50	.02170	1.232	.0906
LiCl	.09	.09	.02558	1.045	.0192
,,	.25	.25	.02394	1.127	.0480
,,	.50	.50	.02160	1.238	.0928
KNO₃	.05	.05	.02658	1.006	.0027
,,	.09	.09	.02640	1.013	.0058
,,	.25	.25	.02610	1.022	.0095
,,	.50	.50	.02558	1.045	.0192
,,	1.00	1.00	.02432	1.097	.0402
NaNO₃	.05	.05	.02648	1.010	.0042
,,	.09	.09	.02634	1.025	.0066
,,	.25	.25	.02658	1.041	.0176
,,	.50	.50	.02452	1.091	.0378
LiNO₃	.05	.05	.02642	1.012	.0053
,,	.09	.09	.02618	1.022	.0094
,,	.25	.25	.02552	1.048	.0204
,,	.50	.50	.02470	1.083	.0345

TABLE III (Continued)

Activity Coefficient f_o of Benzoic acid in Salt Solutions in the Presence of 0.01 Molar Sodium Benzoate at 25°

Salt added to 0.01 molar Na benzoate	Ionic strength salt	Normality salt	Normality benzoic acid	f_o	$+ \log f_o$
KBr	.09	.09	.02608	1.025	.0108
,,	.25	.25	.02562	1.068	.0285
,,	.50	.50	.02364	1.132	.0537
KI	.09	.09	.02642	1.012	.0053
,,	.50	.50	.02528	1.058	.0244
K_2SO_4	.09	.060	.02620	1.021	.0090
,,	.50	.333	.02412	1.119	.0450
$NaClO_4$	.09	.09	.02630	1.027	.0072
,,	.25	.25	.02590	1.033	.0141
,,	.50	.50	.02554	1.060	.0253
$BaCl_2$	.09	.060	.02614	1.023	.0098
,,	.50	.333	.02376	1.126	.0516
$CaCl_2$	.091	.061	.02608	1.025	.0108
,,	.506	.337	.02348	1.139	.0564
$SrCl_2$	.0914	.061	.02604	1.026	.0113
,,	.508	.339	.02346	1.140	.0568
$Ba(NO_3)_2$	.09	.06	.02650	1.009	.0040
,,	.25	.168	.02608	1.025	.0110
,,	.50	.333	.02564	1.043	.0182
$Ca(NO_3)_2$	.0912	.0608	.02646	1.010	.0045
,,	.253	.169	.02624	1.019	.0084
,,	.507	.338	.02582	1.036	.0154
$Sr(NO_3)_2$	.120	.080	.02640	1.013	.0058
,,	.334	.223	.02580	1.037	.0157
,,	.668	.445	.02506	1.067	.0283
$Mg(NO_3)_2$	.0896	.0597	.02646	1.010	.0045
,,	.249	.166	.02594	1.031	.0131
,,	.498	.333	.02534	1.055	.0234

In Figs. 1 and 2, $\log f_o$ is plotted against the ionic strength μ of the salt added. In all cases (except with magnesium nitrate and barium nitrate) a straight line is found as may be expected from the relation:

$$\log f_o = k \mu$$

In practically all cases a close agreement was found with the data of E. Larsson[5] with the exception of potassium bromide, for which salt Larsson gives a

[5] E. Larsson: Z. physik. Chem., **153**, 299, 466 (1931).
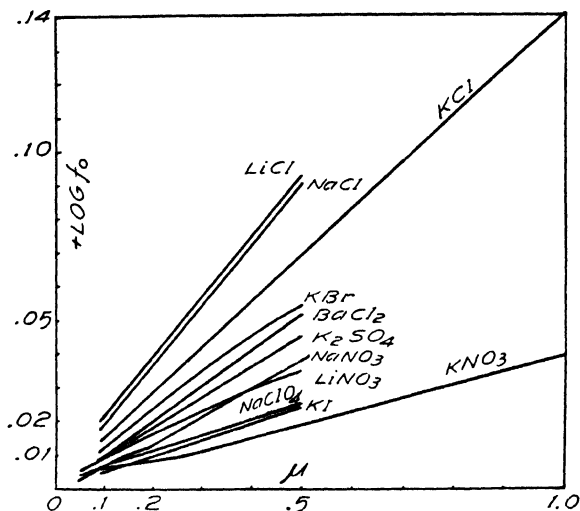
Fig. 1

Salting-out Effect upon Benzoic Acid

value of k equal to 0.07, whereas in the present investigation a value of 0.11 was derived. For salts of divalent cations, Larsson gives the expression: log f_o = kc, where c represents the salt normality. If his figures are recalculated on the basis of ionic strength, the following values of k are found:

	$BaCl_2$	$SrCl_2$	$CaCl_2$	$MgCl_2$
Larsson	0.10	0.11	0.11	0.11
K. and B.	0.10	0.11	0.11	
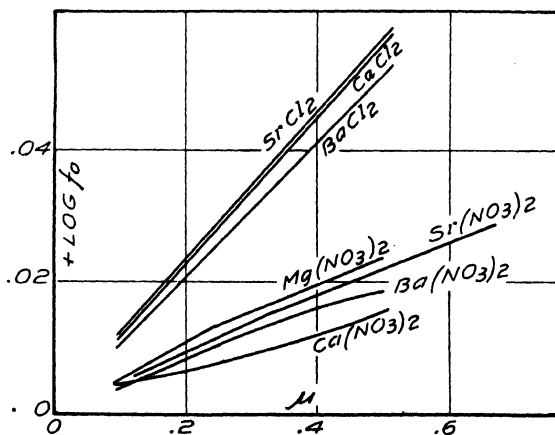
Fig. 2

Salting-out Effect upon Benzoic Acid

A comparison of our figures with others reported in the literature is omitted here (compare, however, thesis of W. Bosch), since E. F. Chase and M. Kilpatrick, Jr.[6] have recently given a complete review of the published data. Our values are in agreement with the results of other reliable investigations.

In the present investigation, it is found that the salting-out effect of the cations decreases in the order:

$$Li > Na > K > Ca > Sr > Mg > Ba$$
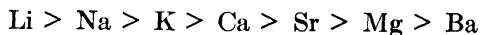
A simple relation between ionic size and salting-out effect as suggested by E. F. Chase and M. Kilpatrick, Jr.[6] does not exist. For the anions, the following order is found:

$$Cl^- > Br^- > SO_4^= > J^- > NO_3^- > ClO_4^-$$
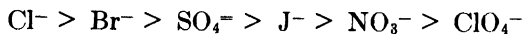
The interpretation of the salting-out effect of cations seems to be fairly well in agreement with the theory of P. Debye and McAulay;[7] greater difficulties, however, are encountered in the interpretation of the anion effect. In the present study it is found that the nitrate and perchlorate ion have an increasing influence on the solubility of benzoic acid. More striking examples of a negative salting-out effect are found in studies of K. Linderström-Lang[8] and especially of H. R. Kruyt and C. Robinson.[9] Kruyt and Robinson[8] attribute the tendency of electrolytes to increase the solubility of non-electrolytes or undissociated organic molecules entirely to a definite orientation of the dipoles of the water molecules around the ions, by which the solvent effect should be increased. The polar organic molecules of the solute, however, also exert an orienting effect on the water molecules, therefore, a most favorable orientation can be expected in a solution of the substance in pure water as a solvent. Any change of the orientation will result in a decrease in the solubility (salting-out effect) and it is hard to see how Kruyt's and Robinson's explanation accounts for the opposite effect observed. In the presence of electrolytes (and especially of cations), the latter will compete with the organic molecules with regard to orientation of the water, resulting in a less favorable orientation of the water molecules around the organic substance or in an increase of the latter's activity. This is the true salting-out effect which decreases in the order $Li > Na > K > Rb > Cs$. Moreover, it seems necessary to assume a direct interaction between the ions in the solution and the dipoles of the solute; resulting in a mutual polarization and deformation. In extreme cases this may lead to a definite complex formation as is the case with benzoate and benzoic acid and otherwise to a decrease of the activity of the solute or increase in solubility. From the studies of Kruyt and Robinson, it seems that the salting-out effect is more likely to be determined by the kind of cations, whereas the deforming effect is governed by the kind of anions present.

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[6] E. F. Chase and M. Kilpatrick: J. Am. Chem. Soc., 53, 2589 (1931); see also Haessler: Thesis, Columbia University, 1929.

[7] Debye and McAulay: Physik. Z., 24, 185 (1923).

[8] K. Linderström-Lang: Compt. rend. trav. lab. Carlsberg, 15, 4 (1924); 17, No. 13 (1929).

[9] H. R. Kruyt and C. Robinson: Proc. Acad. Amsterdam, 29, 1244 (1926).

More extensive studies with different types of organic substances, in which the change of the activities of the ions in the presence of the organic solute are also measured, are necessary before a good understanding of the influence of neutral salts on the activity of undissociated molecules can be obtained.

Summary

1.   The solubility of benzoic acid in water at 25° was found to equal to 0.02775 ± 0.00002 mols per liter, whereas the activity of the acid to be 0.02635 to 0.0264.

2.   The solubility of benzoic acid in sodium benzoate solutions has been determined.   The increase in solubility with increasing salt content is attributed to the formation of anions of double molecules of benzoic acid.   The stability constant of this complex ion has been approximated.

3.   The influence of various neutral salts on the activity of benzoic acid has been determined.   In the interpretation of the experimental data it is assumed that electrolytes exert two effects: (a) a true salting-out effect, mainly governed by the type of cations and resulting in an increase of the activity of the solute.   (b) a mutual deforming effect, mainly governed by the type of anions and resulting in a decrease of the activity of the solute.

Minneapolis, Minn.

THE IONIZATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF THE BENZOATE ION IN PRESENCE OF NEUTRAL SALTS[*]

BY I. M. KOLTHOFF AND WOUTER BOSCH[1]

The hydrogen ion activity was measured in dilute solutions of benzoic acid and sodium benzoate and from the results obtained the ionization constant of the acid was computed by application of the limiting Debye-Hückel expression.

Measurement of the Hydrogen Ion Activity

The activity of the hydrogen ions was measured with the hydrogen electrode. A simple cell was used as described in a previous paper,[2] the quinhydrone electrode in a mixture of 0.01 N hydrochloric acid and 0.09 N potassium chloride served as standard half cell. The cell was refilled every day after cleaning the electrode. The connection between the two half cells was made by a saturated potassium chloride bridge in 3% agar, and no correction has been applied for the liquid junction potential. The measurements have been made in a thermostat at 25° ± 0.05°. The type of hydrogen electrode used in this work gives constant readings with ordinary buffer solutions within two to three minutes. Peculiar difficulties were encountered in the measurement of benzoic acid-benzoate solutions. There was a continuous drift in potential with time, the electrode becoming less and less noble. This irregular behavior could not be attributed to impurities in the hydrogen, as the latter was carefully purified and finally passed over red hot copper or nickel wire. Special experiments were made in order to see whether the effect could be attributed to a hydrogenation of benzoic acid, but no indication of such an action was found. Therefore, it seems that benzoic acid or benzoate exerts a polarizing effect upon the electrode. It was found that the rate of change of the E. M. F. was proportional to the thickness of the layer of platinum black on the electrode, and for this reason the platinum spiral electrodes were covered with a very thin coat of platinum. A 1% solution of pure chloroplatinic acid[3] was used for platinizing, with a current of 20 milliamperes during five minutes. After polarization in 1 N sulfuric acid, the electrode had a grayish appearance. Cleaning and recoating were often necessary, but with the type of electrode described, it was usually possible to obtain constant readings within 15 minutes, although, it should be mentioned, that the final reading was not made unless the potential had been constant for a few hours. In the presence of large concentrations of sodium benzoate (0.25 N or higher) no reliable results

* Contribution from the School of Chemistry, University of Minnesota.
1 Comp. Note 1 in the previous paper; J. Phys. Chem., 36, 1685 (1932).
2 I. M. Kolthoff and Wouter Bosch: Rec. Trav. chim., 46, 434 (1927).
3 E. Wichers: J. Am. Chem. Soc., 43, 1268 (1921).

could be obtained. Owing to the difficulties described, at least three sets of independent measurements with each solution were made; the results are accurate to within 0.01 pH. It may be mentioned that the sluggishness of the electrode is more pronounced in the absence of neutral salts; the latter exert a decidedly favorable effect.

Since the quinhydrone electrode assumes a constant potential very readily, all measurements have also been made with such an electrode. It was found, however, that sodium benzoate changes the activity of the components of the quinhydrone in the solution causing an uncertainty in the calculation. At small benzoate concentrations (below 0.01 N), the effect is small, but at higher benzoate concentrations the figures are no longer reliable. Neither E. Larsson[4] nor M. Kilpatrick and E. F. Chase,[5] who applied the quinhydrone electrode in their work, mention the specific effect of benzoate on the quinhydrone.

The majority of measurements were made in solutions, containing only 0.01 N benzoate in the presence of neutral salts. Quite generally the readings with the quinhydrone electrode gave slightly higher pH values than those with the hydrogen electrode. As a rule the differences were not larger than 0.02, but in the presence of larger amounts of nitrates they were much greater. The differences are partly accounted for by the salt error of the quinhydrone electrode in presence of large concentrations of neutral salts. A special study has been made of this error under the experimental conditions; the work is not completely finished and will be described later.

In Table II the results are given of measurements with the hydrogen as well as the quinhydrone electrode; the figures obtained with the former are used in the calculation of the activity coefficient of the benzoate ion.

The calculation of paH was based on the classical Sörensen equations. The relation between the Sörensen value and the negative logarithm of the hydrogen ion activity paH is given by:

$$paH = pH + 0.037$$

Ionization Constant of Benzoic Acid at 25°

The hydrogen ion activity was measured in dilute mixtures of sodium benzoate and benzoic acid. After correction for the dissociated part of the acid

$$pK' = -\log \frac{[H^+][cB^-]}{[aHB]}$$

in which $[H^+]$ represents the Sörensen value of the hydrogen ion concentration, $[cB^-]$ the benzoate concentration (concentration sodium benzoate plus dissociated part of the acid), and $[aHB]$ the activity of the undissociated acid, pK' was calculated. From this value $pK_o = -\log \dfrac{[H^+]\,[aB^-]}{[aHB]}$ was computed

[4] E. Larsson: Z. physik. Chem., **148**, 304 (1930).

[5] M. Kilpatrick and E. F. Chase: J. Am. Chem. Soc., **53**, 1732 (1931).

with the assumption that in the very dilute solution the simple Debye-Hückel expression holds:

$$\log f_{B-} = -\,0.5\,\sqrt{\mu}$$

$\log f_B$ being the logarithm of the activity coefficient of the benzoate ion. Finally, pK represents the acid exponent after correction for the difference between the Sörensen exponent and paH:

$$pK = pK_0 + 0.037$$

The data are given in Table I.

<div align="center">TABLE I</div>

<div align="center">Ionization Constant of Benzoic Acid at 25°</div>

Concentration sodium benzoate in moles p. l	Concentration benzoic acid in moles p. l	pH	pK′	pK₀	pK
0.05	0.025	4.349	4.047	(4.172)	
0.025	0.025	4.092	4.089	(4.169)	
0.025	0.0125	4.365	4.062	4.141	4.178
0.01	0.01	4.107	4.101	4.151	4.188
0.01	0.005	4.400	4.094	4.144	4.181
0.005	0.005	4.124	4.111	4.146	4.183
0.005	0.0025	4.414	4.103	4.138	4.175
0.0025	0.0025	4.140	4.115	4.140	4.177
0.0025	0.00125	4.431	4.111	4.136	4.173
(0.001	0.001	4.172	4.114	4.130)	

From these and other measurements an average value of pK equal to 4.175 was found corresponding to an ionization constant of 6.7×10^{-5} at 25°. At the same temperature, Jones[6] from conductivity data (not corrected for the difference between activity and concentration) derived a value of 7.0×10^{-5}, whereas Kilpatrick and Chase[5] in a note mention that according to the same method but corrected for activities a constant of 6.31×10^{-5} is found.

<div align="center">

Activity Coefficient of the Benzoate Ions in the Presence of Neutral Salts

</div>

Solutions of 0.01 N sodium benzoate containing the indicated concentrations of neutral salt were saturated with benzoic acid at 25.00°. The paH of these solutions was measured at the same temperature with the hydrogen and quinhydrone electrode. In the further calculations only the hydrogen electrode values were used.

The activity coefficient f_B of the benzoate ions can be readily calculated from the relation,

$$K = \frac{[aH^+]\,[cB^-]f_B}{[aHB]}$$

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[6] Jones: Am. Chem. J., **44**, 159 (1910); **46**, 56 (1912).

TABLE II

Activity Coefficient f_B of the Benzoate Ion in Salt Solutions

Ionic strength of added salt		paH H_2 electr.	paH quinh. electr.	pcB⁻	$-\log f_B$	f_B
.09	KCl	3.622	3.642	1.990	.142	.72
.25	,,	3.601	3.627	1.989	.164	.69
.50	,,	3.627	3.654	1.990	.137	.73
1.00	,,	3.652	3.698	1.990	.112	.77
.09	NaCl	3.601	3.625	1.989	.164	.69
.25	,,	3.559	3.583	1.988	.207	.62
.50	,,	3.524	3.561	1.987	.243	.57
.09	LiCl	3.546	3.567	1.988	.220	.60
.25	,,	3.502	3.532	1.987	.265	.54
.50	,,	3.420	3.461	1.984	.350	.45
.05	KNO₃	3.664	3.656	1.990	.120	.76
.09	,,	3.639	3.644	1.990	.125	.75
.25	,,	3.610	3.650	1.989	.155	.70
.50	,,	3.586	3.650	1.989	.179	.66
1.00	,,	3.568	3.689	1.988	.198	.63
.05	NaNO₃	3.610	3.617	1.989	.155	.70
.09	,,	3.598	3.622	1.989	.167	.68
.25	,,	3.549	3.590	1.988	.217	.61
.50	,,	3.541	3.603	1.988	.225	.60
.05	LiNO₃	3.591	3.600	1.989	.174	.67
.09	,,	3.575	3.590	1.988	.191	.64
.25	,,	3.527	3.563	1.987	.240	.58
.50	,,	3.468	3.529	1.985	.301	.50
.09	KBr	3.615	3.650	1.989	.150	.71
.25	,,	3.622	3.649	1.989	.143	.72
.50	,,	3.561	3.661	1.988	.205	.62
.09	KI	3.610	3.639	1.989	.155	.72
.09	K₂SO₄	3.627	3.625	1.988	.139	.73
.50	,,	3.657	3.617	1.990	.107	.78
.09	BaCl₂	3.578	3.593	1.989	.187	.65
.50	,,	3.427	3.427	1.984	.343	.45
.091	CaCl₂	3.557	3.574	1.988	.209	.62
.506	,,	3.380	3.414	1.982	.392	.41
.091	SrCl₂	3.561	3.590	1.988	.205	.62
.508	,,	3.407	3.444	1.983	.364	.43
.09	Ba(NO₃)₂	3.554	3.563	1.988	.212	.61
.25	,,	3.497	3.508	1.986	.271	.54
50	,,	3.478	3.507	1.986	.290	.51
.091	Ca(NO₃)₂	3.495	3.503	1.986	.273	.53
.253	,,	3.454	3.461	1.985	.315	.48
.507	,,	3.314	3.349	1.980	.460	.35
.12	Sr(NO₃)₂	3.576	3.563	1.988	.190	.65
.334	,,	3.466	3.476	1.985	.303	.50
.668	,,	3.422	3.476	1.984	.348	.45
.09	Mg(NO₃)₂	3.563	3.541	1.988	.203	.69
.249	,,	3.461	3.469	1.985	.308	.56
.498	,,	3.420	3.451	1.984	.350	.44

in which [aHB] is a constant (0.02637 at 25°, see previous paper[1]) since the solution is saturated with benzoic acid and [cB⁻] the benzoate concentration (sodium benzoate + dissociated part of the acid)

$$- \log f_B = - \log K - \log [aHB] - paH - pcB^- = 4.175$$
$$- 1.579 - paH - pcB^-$$

pcB⁻ denotes the negative logarithm of the concentration of the benzoate ions. The results are given in Table II.

Discussion

The change of the activity coefficient of the benzoate ion with the ionic strength of the solution can no longer be represented by the simple Debye-Hückel expression, $-\log f = 0.5\sqrt{\mu}$, because the electrolyte content of the solutions is too high. Only in the case of lithium chloride does the influence of the ionic size seem to be negligibly small (in 0.25 N LiCl: $-\log f_B$ found 0.265; calculated 0.255; in 0.5 N LiCl: $-\log f_B$ found 0.350; calculated 0.357). In most other cases the change of the activity coefficient with the ionic strength can be represented by the more complicated expression:

$$- \log f_B = \frac{0.5\sqrt{\mu}}{1 + A\sqrt{\mu}}$$

in which A is a constant for each salt. In Table 3 examples are given of the application of this equation to solutions in potassium and sodium nitrate respectively. In KNO_3, A = 1.266; in $NaNO_3$, A = 0.340.

TABLE III

Calculated and Experimental Figures of $-\log f_B$ in KNO_3 and $NaNO_3$

	KNO_3			$NaNO_3$	
Total μ	$-\log fB$ exp.	$-\log fB$ calc.	Total μ	$-\log fB$ exp.	$-\log fB$ calc
0.0602	0.120	0.094	0.0602	0.155	0.113
0.1002	0.125	0.113	0.1003	0.167	0.147
0.2602	0.155	0.155	0.2603	0.217	0.217
0.5103	0.179	0.188	0.5103	0.225	0.287
0.010	0.198	0.221			

In most other cases the values of A have not been calculated, since the number of measurements and the concentration range were too small.

A weak point in the measurement of individual ion activities is that uncertainties are introduced on account of the liquid junction potential. E. A. Guggenheim[7] even states that the electric potential difference between two points in different media never can be measured and has not yet been defined in terms of physical realities. It is gratifying, therefore, that in one instance at least, it is possible to check the reliability of our results with those in which no uncertainty is involved. Kilpatrick and Chase[5] derived the mean activity

[7] E. A. Guggenheim: J. Phys. Chem., **33**, 842 (1929).

coefficient of the ions of benzoic acid, $\sqrt{f_H f_B}$, from potentiometric and kinetic measurements in solutions of potassium chloride in presence of some sodium benzoate; no uncertainty caused by the liquid junction potential occurs here. In our work, f_B was experimentally determined, whereas f_H could be calculated in potassium chloride solutions by application of the empirical equation of N. Bjerrum and A. Unmack.[8]

$$- \log f_H = 0.178 \sqrt[3]{c} - 0.154 \, c - 0.003 \quad (25°; \text{KCl at } c = 0.001 - 1.5)$$

From the experimental value of f_B and the calculated value of f_H the mean activity coefficient $\sqrt{f_H f_B}$ was calculated. The data are given in Table IV and compared with those Kilpatrick and Chase. A better agreement can hardly be expected, considering the experimental difficulties in our work.

<div align="center">

TABLE IV

$\sqrt{f_H f_B}$ in KCl Solutions at 25°

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Concentration KCl	K. and B.	$\sqrt{f_H f_B}$ Kilpatrick and Chase Potent.	Kin.
0.09	0.79	0.81	0.805
0.25	0.764	0.80	0.78
0.5	0.80	0.805	0.79
1.00	0.90	0.90	0.93

Considering the figures in Table II, it is evident that the activity coefficient of the benzoate ion passes through a minimum in about 0.25 N potassium chloride. From there on it increases with the ionic strength and seems to become even larger than that of the hydrogen ions. E. Güntelberg and E. Schiödt[9] in their excellent paper, found f_H equal to 1.50 and f_B to 1.93 in 3 N potassium chloride, on the other hand, in the more dilute electrolyte solutions, we find f_B smaller than f_H. In the dilute sodium chloride solutions f_B is smaller than in potassium chloride solutions of corresponding strength. By application of the empirical Bjerrum-Unmack[8] relation in sodium chloride:

$$- \log f_H = 0.161 \sqrt[3]{c} - 0.178 \, c - 0.003 \quad (25°)$$

the following values of $\sqrt{f_H f_B}$ are calculated in sodium chloride solutions: 0.78 in 0.09 N NaCl; 0.74 in 0.25 N NaCl; 0.725 in 0.5 N NaCl. In 3 N NaCl, Güntelberg and Schiödt found a mean activity coefficient of 1.89. From the above, it is evident that the minimum in the activity coefficient of the benzoate ion lies at a higher concentration of sodium chloride than of potassium chloride.

Güntelberg and Schiödt[10] conclude that apparently the benzoate ion can be used for activity studies in which an ion with an extremely high activity coefficient is required. This is true at high salt concentrations; from our

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[8] N. Bjerrum and A. Unmack: Kgl. Danske Videnskab Selskab, 9, 1 (1929).

[9] E. Güntelberg and E. Schiödt: Z. physik. Chem., 135, 393 (1926).

[10] Ref. 9, p. 442.

study it appears that at relatively small ionic strengths the activity coefficient of the benzoate ion is comparable with that of many other monovalent anions. It seems that in relatively dilute solutions the Debye-Hückel expression accounts for the decrease in activity of the benzoate ion; the effect increases with decreasing ionic size: Li > Na > K. In more concentrated solutions, the Debye-Hückel effect is compensated by the salting-out action, which also decreases in the order, Li > Na > K. Therefore, it is quite possible that at very high salt concentrations, the activity coefficient of the benzoate ions is the largest in lithium, smaller in sodium, and the smallest in potassium solutions, or the reverse of that in dilute solutions. The influence of divalent cations on the activity coefficient of the benzoate ion in relatively dilute solutions is of the same order as that of the lithium ions; the effect seems to decrease in the order, Ca > Sr > Mg > Ba, but the differences are relatively small.

In agreement with results of former studies,[11] it is found that the anion effect in relatively dilute solutions is very small.

Summary

1. The quinhydrone electrode no longer gives reliable results in solutions of sodium benzoate. The hydrogen electrode is useful, if the noble metal is covered with a very thin coat of platinum.

2. The ionization constant of benzoic acid is equal to 6.7×10^{-5} at $25°$.

3. The activity coefficient of the benzoate ion in the presence of various electrolytes has been determined. It passes through a minimum at about 0.25 N potassium chloride, at a higher concentration of sodium chloride and still higher concentration of lithium chloride. The cation effect may reverse at high ionic strengths. There is a pronounced cation effect, but a slight anion effect.

Minneapolis, Minnesota.

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[11] I. M. Kolthoff and W. Bosch: Rec. Trav. chim., **47**, 558, 819, 826, 861, 873 (1928); **48**, 37 (1929).

THE MEAN AND INDIVIDUAL ION ACTIVITY COEFFICIENTS OF SILVER BENZOATE IN SALT SOLUTIONS*

BY I. M. KOLTHOFF AND W. BOSCH[1]

The mean activity coefficient, f, of the silver and benzoate ions in silver benzoate has been calculated from solubility measurements of silver benzoate in water and in neutral salt solutions.

$$f = \sqrt{f_{Ag}f_B} = S_o/S$$

in which S_o represents the solubility of silver benzoate at an ionic strength of zero and S the same in the salt solution. The solubility of silver benzoate in water at $25°$ is of the order of 0.01 N. In such a solution, the simple Debye and Hückel expression,

$$-\log f_{Ag} = -\log f_B = 0.5\sqrt{\mu}$$

was applied to derive the value of S_o. In addition, the activity of the silver ions in all solutions was determined directly by means of the silver electrode. From these figures and S_o the activity coefficient of the benzoate ion could be calculated:

$$[a\ Ag^+]\ [a\ B^-] = S_o{}^2$$

The values of f_B could be compared with those found with the hydrogen electrode[2] in the same electrolyte solutions of corresponding ionic strength.

From the measurements of the activity of the silver ions in the saturated solution in water, it appeared that the activity coefficient is about 10% lower than that calculated with the simple Debye and Hückel expression. From this deviation it was concluded that silver benzoate no longer behaves as an ideal strong electrolyte and that part of it in solution is present in the undissociated form. Inner complex formation does not account for the difference as could be concluded from solubility measurements in silver nitrate and sodium benzoate. The activity coefficient of the benzoate ion as calculated from the thermodynamic solubility product $[a\ Ag^+]\ [a\ B^-]$ and the experimental value of $[a\ Ag^+]$ within the experimental error was found to be equal to that computed from measurements with the hydrogen electrode in similar solutions (preceding paper).

Materials used: (Comp. previous paper[2]).

Silver benzoate: Forty grams of pure sodium benzoate were dissolved in distilled water, the solution boiled and slowly added to a boiling solution of 45 grams of C.P. silver nitrate in 500 cc. water. After standing over night,

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the precipitate was collected by suction and washed five times after mixing with the wash water. Finally, the silver benzoate was washed with absolute alcohol and dried at 120° to constant weight.

Tests: Five grams of the preparation were dissolved in boiling water, the silver precipitated with hydrochloric acid and the filtrate evaporated and gently ignited. No residue was obtained, indicating that the salt did not contain inorganic impurities. Moreover, the silver content was determined gravimetrically: 47.05 and 47.00% Ag (calc. 47.13%).

Silver nitrate: Although labelled as C.P. and "maximum impurities less than 0.022%," the product appeared to contain more impurities besides 0.15% water. The salt was melted in a silica dish, kept at the melting point for about 15 minutes and poured upon a porcelain plate. The crust was powdered and dissolved in water, leaving a black residue. After recrystallization, the crystals were heated to the melting point in order to remove water. The purity was tested by potentiometric titrations with pure potassium chloride.

Solubility of Silver Benzoate in Water and in Salt Solutions

In all cases the solutions with the solid body were rotated for at least three days in a thermostat at 25.00° ± 0.01° before the samples were analyzed. This time of shaking was adequate to secure a saturated solution; after rotating for 25 consecutive days the same figures were found. The silver content of the samples was determined by potentiometric titration with pure potassium thiocyanate as a reagent. The latter was standardized potentiometrically against pure silver nitrate which had been checked again against potassium chloride. As an average of 12 independent analyses (different bottles) a solubility of silver benzoate in water equal to 0.01162 ± 0.00002 moles per liter was found at 25°. Assuming that in this solution, the simple Debye and Hückel relation holds, it is found:

$$-\log f_{A_g} = -\log f_B = 0.5\sqrt{0.01162} = 0.054 \text{ or } f = 0.883$$

and, $\quad S_o = 0.01162 \times 0.883 = 0.01026$

The results are given in Table I. In the last column $-\log f$ has been calculated for potassium and calcium nitrate solutions by means of the Debye-Hückel expression:

$$-\log f = \frac{0.5\sqrt{\mu}}{1 + A\sqrt{\mu}}$$

In potassium nitrate, A is found to be equal to 1.182, in calcium nitrate to 0.551. E. Larsson and B. Adell[3] at 18° found in potassium nitrate up to a concentration of 3 N the following relation:

$$-\log f = \frac{0.5\sqrt{\mu}}{1 + 1.42\sqrt{\mu}} - 0.005$$

F. H. McDougall[4] calculated from solubility measurements of silver acetate

[3] E. Larsson and B. Adell: Z. anorg. allgem. Chem., **196**, 354 (1931).

[4] F. H. McDougall: J. Am. Chem. Soc., **53**, 1392 (1930).

in potassium nitrate solutions up to an ionic strength of one, a value of A between 1.408 and 1.479.

TABLE I

Mean Activity Coefficient f of Silver and Benzoate Ions of Silver Benzoate in Salt Solutions at 25°

Ionic strength and added salt		Solubility silver benzoate	Total Ionic strength	−log f	f	−log f. calc. Debye-Hückel
Water		.01162	0.01162	.054	.88	
S°		.01026				
.05	N KNO₃	.01298 N	.0630	.1021	.79	0.097
.09	" "	.01369 "	.01040	.1253	.75	0.1253
.10	" "	.01366 "	.1137	.1243	.75	0.121
.25	" "	.01483 "	.2648	.1600	.69	0.160
.50	" "	.01590 "	.5159	.1903	.64	0.194
.50	" NaNO₃	.01628 "	.5163	.2005	.63	
.50	" LiNO₃	.01648 "	.5165	.2058	.62	
.50	" Ba(NO₃)₂	.01697 "	.5170	.2185	.60	
.498	" Mg(NO₃)₂	.01759 "	.5156	.2341	.58	
.668	" Sr(NO₃)₂	.01784 "	.6858	.2402	.57	
.253	" Ca(NO₃)₂	.01633 "	.2693	.2018	.63	0.2018
.507	" " "	.01834 "	.5253	.2553	.56	.2059
1.013	" " "	.02079 "	1.034	.3067	.49	0.326

The results of the solubility measurements in sodium benzoate and silver nitrate solutions respectively are given in Tables VI and VII and will be discussed later.

The Potentiometric Determination of the Silver Ion Activity

From studies reported in the literature,[5] it follows that the readings with the silver electrode depend greatly upon the kind of electrode used and the condition of the solutions; it is hard to obtain reproducible results. In our case it was of primary importance to obtain results reproducible to within at least 0.5 millivolt. A special study of the silver electrode, therefore, had to be made. Carmody[5] states that the following factors are of influence on the potential of the electrode: "cyanide ion adsorbed by the silver plated electrode, time of electrolyzing, light, and concentration of chloride." To this may be added a very important factor: influence of air. After various types of electrodes had been tried, Carmody's plating procedure was finally adopted.

Platinum gauze electrodes of cylindrical shape with a diameter of 0.5 cm., a height of 1 cm., and a mesh of 52 to the inch (wire diameter, 0.01 mm.)

[5] Comp. e.g. Randall and Young: J. Am. Chem. Soc., 50, 990 (1928); W. R. Carmody: 51, 2901 (1929); Noyes and Ellis: 39, 2533 (1917); Lewis, Brighton and Sebastian: 39, 2245 (1917); Brester: Rec. Trav. chim., 46, 328 (1927); Güntelberg: Z. physik. Chem., 123, 199 (1926); Brönsted: 50, 481 (1904); Linhart: J. Am. Chem. Soc., 41, 1175 (1919); Halla: Z. Elektrochemie, 17, 179 (1911); Jahn: Z. physik. Chem., 33, 545 (1900).

after washing were cleaned with boiling nitric acid and ignited to a dull red heat. As plating bath a 1 N solution of potassium silver cyanide prepared by adding 13 grams of potassium cyanide dissolved in 100 cc. water to a solution of 18 grams silver nitrate in 100 cc. water was used. The electroplating was carried out in a black painted H-shaped cell with a current of one milliampere during 18 hours, using a strip of pure silver as anode. After boiling three times with distilled water, the electrodes were anodically covered with a thin layer of silver chloride by electrolyzing them for twenty minutes in one N hydrochloric acid with a current strength of 3.5 milliamperes. Finally, they were washed with very dilute sodium chloride solution and water, and kept in the dark at all times during preparation and measurements.
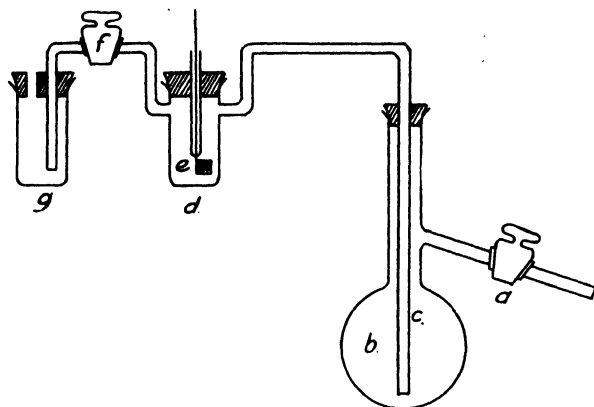
Fig. 1

Although this type of electrode gave better results by far than any of the other types tried, they still were not quite satisfactory, especially, not in very dilute silver nitrate solutions. In all solutions containing air, irregular fluctuations were observed with time. For example, the following readings were made in 0.1 N silver nitrate, using the quinhydrone electrode in 0.01 N hydrochloric acid and 0.09 N potassium chloride as a reference electrode: E.M.F. after 1/2 hour 0.1542 V; after 1 hour 0.1542; 2 hours 0.1549; 3 hours 0.1551; 12 hours 0.1571. With other electrodes, slightly different values were found.

In order to get constant and reproducible results it appeared to be necessary to remove all dissolved gases from the solutions. This was done by evacuation in a similar way as Brester[5] has suggested.

The final design of the apparatus is given in Fig. 1, and resembles that of Brester closely.

The apparatus consists of a vessel, d, in which the silver plated platinum gauze electrode, e, is fixed by means of a one hole rubber stopper. The long tube, c, projects into the distilling flask, b. At the left side is a wide tube which is filled with a glass stopcock of 3 mm. bore, which in turn leads into the vessel, g. This end is closed by means of a piece of rubber tubing and a

screw clamp; the distilling flask filled with a suitable amount of the liquid to be measured and the apparatus put together as shown in the illustration with the exception of the vial, g, which is connected later.

After opening of the stopcock, f, suction was applied at the tube, a, by means of an oil vacuum pump. The air was then admitted through the tube, filling the entire apparatus with liquid. This operation was repeated three times, decreasing the pressure each time until the liquid in the vessel started boiling. This was necessary to remove air bubbles adhering to the electrode and to the walls of the vessel as thoroughly as possible. The distilling flask was then removed and the electrode vessel closed at both sides, c, and g, and immersed in the thermostat at 25.00° over night. The next morning the tap, f, was closed and the tubes, c and g, opened. The latter was then connected with the vial, g, which had been filled with a concentrated potassium chloride solution, while the other end, c, was attached to a Kipp apparatus, filled with air. Owing to the pressure it was possible to make a fresh contact in the tube "g" between the silver solution and chloride solution. There was a small turbidity at the exit of this tube, but as it was wide (4 mm. inside diameter), there was no danger of obstruction. The necessary contact with the reference electrode (quinhydrone in standard acid mixture) was made with a 2% agar bridge, saturated with KCl at 25°C (approximately 3.5 N).

The amount of liquid evaporating during the evacuation was negligibly small as was shown by special experiments in which a trap immersed in ether and solid carbon dioxide was placed between the distilling flask and the oil pump. After three successive evacuations, the volume of condensed liquid in the trap was less than one drop, which can be neglected in a total volume of 50 to 70 cc.

With the apparatus described, it was possible to obtain results reproducible within 0.1 to 0.2 milli volt, even in solutions as dilute as 0.001 N silver nitrate. Three electrodes were always placed in the same solution and the readings accepted only if the agreement was within 0.2 to 0.3 milli volt. In the presence of benzoate, it is much more difficult to get constant and reproducible results as will be mentioned later. It is peculiar that the benzoate ion exerts an unfavorable influence upon the silver electrode as well as the hydrogen electrode.

The Normal Potential of the Silver Electrode

The potential of the silver electrode was measured in silver nitrate solutions using the quinhydrone electrode in 0.01 N hydrochloric acid and 0.09 N potassium chloride as a reference electrode. The values of the E.M.F. reported in Table II give the average of at least three determinations which agreed with 0.2 milli volt. The normal potential against the above electrode was calculated by means of the equation:

$$E_0 = E + 0.0591 \log \frac{1}{[c\ Ag^+]f_{Ag}}$$

in which E is the E.M.F. measured, [c Ag$^+$] the silver nitrate concentration and f$_{Ag}$ the activity coefficient of the silver ions. The latter value was found by application of the simple Debye and Hückel expression:

$$-\log f_{Ag} = 0.5\sqrt{[c\ Ag^+]}$$

TABLE II

The Normal Potential of the Silver Electrode at $25°$

Conc. AgNO$_3$ moles p. l	E.M.F. in Volts	$-\log f_{Ag}$ calculated	f_{Ag} calculated	E$_0$
0.0504	0.1443	(0.1123)	(0.77)	(0.2276)
0.0402	0.1386	0.1002	0.79	0.2270
0.0202	0.1223	0.071	0.85	0.2267
0.0101	0.1056	0.050	0.89	0.2268
0.0050	0.0891	0.035	0.92	0.2272
0.0030	0.0752	0.027	0.94	0.2268
0.0020	0.0658	0.022	0.95	0.2266
0.0010	0.0480	0.016	0.96	0.2263
0.000			Average	0.2269

From the constancy of E$_0$ it follows that this simple expression can be applied in the case of silver nitrate up to concentrations of 0.05 N; at higher concentrations the calculated value is smaller than the experimental as could be expected.

The average value of E$_0$ is 0.2269 $\pm$ 0.0002 volts at $25°$, or the normal potential of the silver electrode against the normal hydrogen electrode E$_{oH}$ = 0.8030 $\pm$ 0.0002 volt. It seems to the authors that this value is more accurate than any of the others reported in the literature.

In Table III the activities of the silver ions in 0.01 N silver nitrate in the presence of various neutral salts as determined with the silver electrode are reported. Similar measurements have been made in silver benzoate solutions instead of silver nitrate (comp. Table IV), and it was interesting to compare the results.

TABLE III

f$_{Ag}$ in 0.01 N Silver Nitrate in the Presence of Neutral Salts

Salt added	Ionic strength salt p. l	E.M.F. in volts	a$_{Ag}$	f$_{Ag}$	$-\log f_{Ag}$
KNO$_3$	.05	.0998	.00706	.70	.155
,,	.10	.0982	.00664	.66	.182
,,	.25	.0954	.00596	.59	.228
,,	.50	.0941	.00566	.56	.252
NaNO$_3$	.50	.0975	.00647	.64	.193
LiNO$_3$	.50	.0992	.00690	.68	.166
Ba(NO$_3$)$_2$	.50	.0980	.00659	.65	.185
Ca(NO$_3$)$_2$	.507	.0986	.00675	.67	.175
Sr(NO$_3$)$_2$	.668	.0987	.00678	.67	.173
Mg(NO$_3$)$_2$	.498	.0992	.00690	.68	.166

The good reproducibility of all readings gave confidence in the use of the silver electrode for measurements of f_{Ag} in silver benzoate solutions. However, in a saturated solution of silver benzoate in water it was found that the reproducibility was much less than in silver nitrate solutions. Addition of neutral salts had a beneficial effect.

In the saturated solution in water values of E were measured between 0.1068 and 0.1082 volt, the average of seven measurements being 0.1073 ± 0.0005 volt. The total concentration of the silver ions in the saturated solution at 25° is 0.01162 equivalents per liter, whereas from the potentiometric measurement a silver ion activity of 0.009462 is found. Therefore, in the saturated solution f_{Ag} is equal to $\dfrac{0.009462}{0.01162} = 0.813$, whereas by application of the simple Debye and Hückel expression (comp. Table I) a value of 0.883 was calculated. The difference is much larger than can be accounted for by the experimental error and the conclusion is drawn *that silver benzoate in a saturated solution in water no longer behaves as an ideal strong electrolyte.* This conclusion is supported by the following work.

In Table IV the results are given of the measurements of the silver ion activity in saturated solutions of silver benzoate in the presence of neutral salts. The indicated amounts of salt were added to the water and the solutions saturated with silver benzoate.

TABLE IV

Influence of Salts upon the Activity of the Silver Ions in a Saturated Solution of Silver Benzoate

Salt added	Ionic strength salt p. l	E.M.F.	a_{Ag}	[c Ag⁺]	f_{Ag}	$-\log f_{Ag}$
Water		.1073	.00946	0.01162	.81	.090
KNO₃	.05	.1052	.00873	.01298	.67	.172
,,	.10	.1048	.00859	.01366	.63	.201
,,	.25	.1039	.00830	.01483	.56	.252
,,	.50	.1047	.00815	.01590	.54	.269
NaNO₃	.50	.1077	.00962	.01628	.59	.228
LiNO₃	.50	.1097	.01040	.01648	.63	.200
Ba(NO₃)₂	.50	.1100	.01052	.01697	.62	.208
Mg(NO₃)₂	.498	.1110	.01094	.01759	.62	.206
Sr(NO₃)₂	.668	.1114	.01112	.01784	.62	.206
Ca(NO₃)₂	.253	.1098	.01045	.01633	.64	.194
,,	.507	.1115	.01114	.01834	.61	.216
,,	1.013	.1136	.01211	.02079	.58	.234

In all cases the activity coefficient of the silver ions in silver benzoate solutions is smaller than the same in silver nitrate solutions of corresponding strength (comp. Tables III and IV), which could be expected if the silver benzoate were not completely ionized. From the mean activity coefficient, $f = \sqrt{f_{Ag}f_B}$ as reported in Table I and the values of f_{Ag} as given in Table IV, f_B can be calculated.

However, in the derivation of f (Table I), it has been assumed that silver benzoate in its saturated solution behaves as an ideal strong electrolyte and that $f_{Ag} = f_B = 0.883$. Actually, f_{Ag} is equal to 0.813 and in such a dilute solution a similar value can be accepted for f_B. Therefore, S_o of silver benzoate is not equal to 0.01162×0.883, but to $0.01162 \times 0.813 = 0.00945$, moreover, all values of f should be multiplied by $0.813/0.883 = 0.920$, and all values of $-\log f$ should be increased by 0.036. In the calculation of f_B this correction has been applied to $-\log f$ in Table I: $-\log f_B = -2 \log f + \log f_{Ag}$. The results are given in Table V.

2 log f is taken from Table I, but corrected for the above difference; $-\log f_{Ag}$ is taken from Table IV. $-\log f_B$ as given in the fifth column is calculated with the aid of the above equation. In the sixth column values of $-\log f_B$ as found in solutions of sodium benzoate, benzoic acid and neutral salts[6] of similar composition and ionic strength are reported. Finally, the last column gives the difference between the two values of $-\log f_B$ which have been determined in an entirely different way. Considering all the experimental difficulties the agreement between the two columns may be considered as excellent and it supports the conclusion that silver benzoate in its saturated solution is not completely ionized.

TABLE V

$-\log f_B$ derived from Measurements with the Silver Electrode and the Hydrogen Electrode Respectively

Salt added	Ionic strength salt added p. l	$-2 \log f$ (Table I, corrected)	$-\log f_{Ag}$ (Table IV)	$-\log f_B$ from f and f_{Ag}	$-\log f_B$ from H$_2$ electrode	$\Delta(\log f_B)$
KNO$_3$	0.05	0.276	0.172	0.104	0.120	-0.016
,,	0.25	0.392	0.252	0.140	0.155	-0.015
,,	0.5	0.453	0.269	0.184	0.179	$+0.005$
NaNO$_3$	0.5	0.473	0.228	0.245	0.225	$+0.02$
LiNO$_2$	0.5	0.484	0.200	0.284	0.301	-0.017
Ba(NO$_3$)$_2$	0.5	0.509	0.208	0.301	0.290	$+0.011$
Mg(NO$_3$)$_2$	0.498	0.540	0.206	0.334	0.350	-0.016
Sr(NO$_3$)$_2$	0.668	0.552	0.206	0.346	0.348	-0.002
Ca(NO$_3$)$_2$	0.253	0.476	0.194	0.282	0.315	-0.033

This is also in harmony with results of conductivity measurements. It was found that at 25° the conductivity coefficient $\alpha = \Lambda_c/\Lambda\infty$ in 0.01 N silver benzoate is equal to 0.875, in 0.01 N sodium benzoate to 0.919, whereas in potassium chloride of the same concentration it is equal to 0.947. Anyhow, the results of this study show that one has to be careful in considering even uni-valent salts of organic acids as ideal strong electrolytes.

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[6] Comp. I. M. Kolthoff and W. Bosch; J. Phys. Chem., **36**, 1695 (1932).

Finally, in Tables VI and VII the solubility of silver benzoate in silver nitrate and sodium benzoate solutions respectively, has been given. Moreover, [a Ag$^+$] has been determined with the silver electrode and f and f$_B$ calculated:

$$f = \sqrt{\frac{S_o{}^2}{[c\ Ag^+]\ [cB^-]}}$$

$$f_B = \frac{S_o{}^2}{[a\ Ag^+]\ [cB^-]}$$

assuming that S$_o$ is equal to 0.00945.

By comparing the figures of f in the two tables, it is evident that the mean activity coefficient of the silver benzoate is the same at the same excess of silver nitrate and sodium benzoate respectively. The individual activity coefficients of the silver and benzoate ions, however, are quite different. The values of f$_{Ag}$ in the presence of an excess of silver nitrate (Table VI) agree closely with those in silver nitrate at corresponding ionic strength (see Table II). It appears then that the activity coefficient of the benzoate ions in the presence of an excess of silver nitrate is extremely small; the values are even lower than calculated on the basis of the simple Debye-Hückel expression.

In the presence of an excess of sodium benzoate extremely low values of f$_{Ag}$ are measured and abnormally high values of f$_B$ are calculated (of the order of 1). Since the potentiometric measurements in the presence of an excess of benzoate are extremely difficult and not quite reproducible the values of f$_{Ag}$ and f$_B$ do not seem to be quite reliable. More work is required before definite conclusions can be drawn and the figures of f$_{Ag}$ and f$_B$ are omitted in Table VII.

From all experimental data given in this paper, however, it is evident that silver benzoate does not behave as an ideal strong electrolyte.

TABLE VI

Solubility of Silver Benzoate in Silver Nitrate Solutions and Values of f, f$_{Ag}$ and f$_B$ at 25°

Conc. silver nitrate moles p.l.	Conc. silver benzoate moles p.l.	f	E.M.F. in Volts	[c Ag$^+$]	[a Ag$^+$]	[c B$^-$]	f$_{Ag}$	f$_B$
0.00	0.01162	0.813	0.1073	0.01162	0.0095	0.116	(0.81)	(0.81)
0.01	.00786	.798	.1128	.01786	.0148	.0079	.83	.77
0.02	.00576	.777	.1272	.02576	.0206	.0058	.80	.75
0.03	.00447	.760	.1346	.03447	.0274	.0045	.79	.73
0.04	.00392	.721	.1412	.04392	.0355	.0039	.81	.64
0.05	.00328	.716	.1456	.05328	.0421	.0038	.79	.65
0.10	.00248	.593	.1605	.1025	.0753	.0025	.75	.48

TABLE VII

Solubility of Silver Benzoate in Sodium Benzoate Solutions
and Values of f at 25°

Conc. sodium benzoate moles p. l.	Conc. Silver benzoate moles p. l.	f	$[c\ Ag^+]$	$[c\ B^-]$
0.00	0.01162	0.813	0.01162	0.1162
0.01	.00816	.777	.00816	.01816
0.02	.00585	.769	.00585	.02585
0.03	.00477	.734	.00477	.03477
0.04	.00396	.717	.00396	.04396
0.05	.00347	.694	.00347	.05347
0.10	.00240	.603	.00240	.1024

Summary

1. The solubility of silver benzoate in water at 25° is 0.01162 + 0.00002 moles per liter. *The salt does not behave as an ideal strong electrolyte and is not completely ionized in its saturated solution.* It is calculated that $[a\ Ag^+] \times [a\ B^-] = 8.9 \times 10^{-5}$ at 25°.

2. The mean activity coefficients and the individual ion activity coefficients of silver benzoate have been determined in various salt solutions. The computed values of the activity coefficient of the benzoate ion correspond with those derived from measurements with the hydrogen electrode in the system benzoic acid-sodium benzoate-neutral salt, only on the assumption that silver benzoate is not completely ionized in its saturated solution.

3. A special study has been made of the silver electrode. The normal potential of the silver electrode as measured against quinhydrone in 0.01 N hydrochloric acid and 0.09 N potassium chloride as reference electrode is 0.2269 ± 0.0002 volt, or $E_{oH} = 0.8030 ± 0.0002$ volt at 25°.

4. The activity coefficient of silver ions in 0.01 N silver nitrate in the presence of neutral salts has been determined.

PERHALIDE EQUILIBRIUM IN NON-AQUEOUS SOLUTIONS

BY ERNEST A. DANCASTER

The increased solubility of the halogens in water brought about by the presence of halide acids or salts has long been the subject of much speculation and experimental work, the most fruitful method of investigation being by means of the application of the Distribution Law of Nernst. This method was first used for the purpose by Roloff[1] but Jakowkin[2] was the first to make a systematic study of the equilibrium involved, and the view usually accepted at the present time, that the halogen dissolved in a dilute aqueous solution of a metallic halide is present chiefly in the form of tri-halide is based mainly upon his work, and that of his successors. This investigator assumed that the thermal dissociation of the tri-iodide takes place according to the equilibrium

$$MI.I_2 \rightleftharpoons MI + I_2.$$
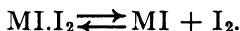
and further assumed that both the iodide atoms of a bivalent halide are equally active in combining with the dissolved iodine. The corresponding equilibrium constant is given by the expression

$$K = \frac{\{na - (b - x)\}x}{b - x},$$

where n is the valence of the metal under consideration, a is the original concentration of the halide, b is the concentration of the free halogen in the aqueous layer as determined by titration, and x is the concentration of the free uncombined halogen, all concentrations being given in gramme molecules per litre. Jakowkin's investigations have been confirmed and extended by Bray and Mackay,[3] Fedotieff[4] and others. Herz and Kurzer[5] studied the case of barium iodide and iodine, keeping the concentration of the iodide constant, while they varied that of the iodine. They, however, assumed that one only of the two iodine atoms of the barium iodide combined with iodine, according to the equilibrium

$$BaI_4 \rightleftharpoons BaI_2 + I_2,$$
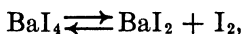
the corresponding equilibrium constant being given by the expression

$$K = \frac{\{a - (b - x)\}x}{b - x},$$

employing the same equation, Herz and Bulla[6] investigated the iodides of calcium, strontium and barium. Although the values of K calculated from this equation, exhibit a fair degree of constancy it has been shown by Van

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[1] Z. physik. Chem., **13**, 341 (1894).
[2] Z. physik. Chem., **13**, 539 (1894); **18**, 585 (1895); **20**, 19 (1896).
[3] J. Am. Chem. Soc., **32**, 1207 (1910).
[4] Z. anorg. Chem., **69**, 122 (1910).
[5] Z. Electrochemie, **16**, 869 (1910).
[6] Z. anorg. Chem., **71**, 25 (1911).

Name and Brown[1] that a much greater constancy is obtained when Jakowkin's equation is used. These investigators, therefore, conclude that the latter is the correct one, a conclusion that has been confirmed by Pearce and Eversole.[2] Van Name and Brown have also shown that the constant, calculated by Jakowkin, holds not only for the halides of the bivalent metals, but also for the trivalent metal lanthanum. These investigators made a distinct advance by showing that the bromides and iodides of mercury and cadmium behave abnormally, while all the other halides which they examined, or which had been previously examined, gave a normal value for the dissociation constant. They also calculated the percentage of complex molecules and ions, on the assumption that these do not combine with the halogen. Although Jakowkin has studied the dissociation of a few perhalogen compounds of the type $XClBr_2$, $XClI_2$ and $XBrI_2$, very little work had been done on the perhalogen compounds containing two different halogens, until Priyadaranjan Rây and Pulin Vihari Sarkar[3] investigated the formation and dissociation of the perhalogen acids $HClBr_2$, $HClI_2$ and $HBrI_2$ in aqueous solution, and Dancaster[4] studied the chloro-perbromide equilibria, and found that the chloro-perbromides of mercury and cadmium exhibited abnormalities to those shown by the perbromides and periodides of these metals, and showed that Jakowkin's constant held for the trivalent metal aluminium. None of the halides examined, except those of mercury and cadmium, showed any abnormality. Pierce and Eversole[5] investigated the distribution of iodine between carbon tetrachloride and aqueous solutions of barium iodide at $25°C$. The concentrations were determined on the basis of molecules per 1000 grammes of solvent, with the purpose of eliminating the effects due to variations in the amount of solvent. These investigators found that the distribution ratio of iodine between water and carbon tetrachloride is independent of the concentration of the iodine for the range of concentrations used. This result is at variance with that found by Jakowkin, and as all the work done by means of the distribution method of determining the dissociation constants of the perhalides in aqueous solution has been based upon Jakowkin's figures, Pearce and Eversole's results are of importance, and should be either confirmed or refuted. From the results obtained Pearce and Eversole conclude that the tri-iodide is the only periodide present in dilute solutions unsaturated with iodine, whilst a mixture of the tri-iodide and penta-iodide is present in solutions saturated with iodine. Dawson and his co-workers[6] investigated the existence of periodides in nitrobenzene, and other nitro-organic aromatic compounds, and inferred from the results obtained that periodides as high as the enneaiodide, KI_9, are probably present in the solutions. Jones[7] investigated the existence of hydrogen perbromide in acetic acid and aqueous-acetic acid solutions at $15°C$. Most of the investigations have been carried

[1] Am. J. Sci., [iv], **44**, 1051 (1917).
[2] J. Phys. Chem., **28**, 245 (1924).
[3] J. Chem. Soc., **121**, 1449 (1922).
[4] J. Chem. Soc., **125**, 2038 (1924).
[5] Loc. cit.
[6] J. Chem. Soc., **79**, 238 (1901); **81**, 524 (1902); **85**, 79 (1904); **93**, 1308 (1908).
[7] J. Chem. Soc., **99**, 403 (1911).

out at 25°C., and there are very few figures available for the dissociation constant at other temperatures. Also, with the exception of the work of Dawson and his co-workers and of Jones, the investigations have been limited to aqueous solutions.

The objects of the present investigation were (1) to develop a method for the determination of the thermal dissociation of perhalides in non-aqueous solutions, (2) to ascertain whether the halides of mercury and cadmium in such solutions showed corresponding abnormalities to those shown in aqueous solution, (3) to extend the number of halides investigated so as to include those which cannot be employed in aqueous solution, (4) to ascertain whether or not any of these halides exhibit any abnormalities such as those shown by mercury and cadmium, and (5) to carry out investigations in aqueous and non-aqueous solutions at various temperatures in order to ascertain whether or not the dissociation constant varied with the temperature, and to compare the values of K obtained in aqueous and non-aqueous solutions. The work, of course, necessitated the determination of the distribution of bromine between the organic solvent and air at the temperature employed, and of the distribution ratio of bromine between water and carbon tetrachloride at temperatures other than 25°C. Jakowkin's values were taken for the distribution of bromine between water and carbon tetrachloride at 25°C.

Experimental.—The materials employed were the purest obtainable, and were usually of A. R. quality. The bromides of tin and aluminium were prepared from bromine and the respective metals. All materials were submitted to further purification. A. R. acetic acid gave very erratic results, owing to reaction with the bromine, but after purification by means of the method of Orton and Bradfield[1] the purified acid was not appreciably affected by bromine, and the results obtained were consistent.

The method employed for the determination of the dissociation constant in an organic liquid was a modification of that employed by Jakowkin for the determination of the constant in aqueous solution, in which the distribution of a halogen between an organic solvent, or a solution of a halide in the organic solvent, and the atmosphere above the liquid is determined, instead of the distribution of the halogen between water, or an aqueous solution of a halide, and an organic liquid. It was necessary that the organic liquid chosen for this purpose should be a fairly good solvent for the halides used, and a very good solvent for bromine, and that this liquid should not be attacked by bromine at the temperature of the experiments. Glacial acetic acid was found to satisfy these conditions better than any other organic liquid tried, and this acid was, therefore, used throughout the investigation, although the solubility of some of the halides was found to be very small. For this reason sodium chloride and aluminium chloride could be investigated in very dilute solution only, and cadmium chloride could not be used because it was found to be practically insoluble in acetic acid. It was found possible to obtain solutions of from 0.02 to 0.1 gramme molecule per litre with all the other halides employed, and the chlorides of tin and antimony, and the bro-

[1] J. Chem. Soc., **125**, 960 (1924).

mide of tin, were found to be very soluble. Titanium chloride could not be employed because it was found to decompose acetic acid with explosive violence as soon as the two liquids were brought into contact. The halides investigated were the chlorides of lithium, sodium, potassium, mercury, iron, aluminium, tin and antimony, and the bromides of sodium, potassium, mercury, cadmium, aluminium and tin. At the time this method was developed the author was unaware that it had been previously employed, but has since discovered that the same method, differing only in details, was used by Jones[1] for the determination of solubility coefficients.

The method employed for the determination of the dissociation constant in aqueous solution was the usual one, in which the aqueous solution and the solution of halogen in an organic solvent are shaken up in a stoppered bottle, and left in the thermostat to settle out. The amount of bromine in each layer is then determined by titration with sodium thiosulphate.

The determination was carried out as follows. A solution of bromine in acetic acid, or in a solution of a halide in acetic acid, was placed in a wash bottle fitted with a ground-glass stopper, through which passed the inlet and outlet tubes, and the flask was left in the thermostat until the contents had attained the required temperature. 10 c.c. of the solution were then withdrawn by means of a pipette, run into an excess of potassium iodide solution, largely diluted with water, and the liberated iodine titrated with N/20 sodium thiosulphate. An aqueous solution of potassium iodide was placed in a second wash bottle, and the two wash bottles were joined up to the rest of the apparatus, consisting of a tower containing calcium chloride and soda lime, an air chamber, an aspirator provided with a thermometer to register the temperature of the interior, and a manometer. The air chamber and the first wash bottle were kept within the thermostat. About 2 litres of air were slowly drawn through the apparatus. This air was dried and freed from carbon dioxide while passing through the tower, and brought to the temperature of the thermostat in the air chamber. The purified and heated air then bubbled through the solution in the first wash bottle, and the bromine laden air passed through the potassium iodide solution, liberating an equivalent amount of iodine which remained in solution in the second wash bottle. At the end of the experiment a second 10 c.c. of the solution was withdrawn from the first wash bottle and titrated. The first and second titrations gave the initial and final bromine concentrations, and the mean of these two results was taken as the average bromine content of the solution during the experiment. The liberated iodine was also titrated in order to ascertain the amount of bromine removed, and the concentration of bromine in the atmosphere in contact with the solution was calculated from the volume of air passed through the apparatus, after applying corrections for temperature and pressure, and also for the vapour of water in the aspirator, the vapour pressure of acetic acid in the first wash bottle, and the volume of bromine in the atmosphere in contact with the solution.

The distribution coefficient of bromine between acetic acid and the atmosphere in contact with the solution was determined at $15°C$, $20°$, $25°$,

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[1] Loc. cit.

30° and 40°. This atmosphere, of course, consists of a mixture of air, acetic acid vapour and bromine vapour in equilibrium with the liquid, but it will, in this paper be described simply as air. The results are shown in Table I, where B gives the concentration of the bromine in acetic acid, and G gives the concentration of the bromine in air. In both cases the concentrations are given in gramme molecules per litre.

TABLE I

The Distribution of Bromine between Acetic Acid and Air

	B	G	Ratio
At 40°	0.39274	0.001422	276.2
	0.26092	0.0009312	280.2
	0.23134	0.0008295	278.9
	0.15791	0.0005640	280.0
	0.12658	0.0004583	276.2
	0.12077	0.0004333	278.7
	0.10969	0.0003982	275.5
	0.10331	0.0003930	277.0
	0.09808	0.0003537	277.3
	0.08414	0.0003049	275.8
	0.06863	0.0002469	278.0
	0.04696	0.0001706	275.3
		Average	277.4
At 30°	0.29630	0.0007056	419.9
	0.23382	0.0005577	419.2
	0.21410	0.0005102	419.6
	0.17931	0.0004269	420.0
	0.16350	0.0003922	416.9
	0.14762	0.0003518	419.6
	0.13659	0.0003284	415.9
	0.12125	0.0002894	418.9
	0.11390	0.0002713	419.8
	0.09804	0.0002334	420.0
	0.07906	0.0001885	419.4
	0.05506	0.0001311	420.0
	0.04926	0.0001182	416.7
	0.04017	0.00009589	418.9
		Average	419.1
At 25°	0.89242	0.001707	522.8
	0.64175	0.001237	518.9
	0.42800	0.0008228	520.2
	0.22809	0.0004400	518.4
	0.18107	0.0003498	517.6
	0.15354	0.0002951	520.3
	0.14911	0.0002880	517.7
	0.13846	0.0002673	518.0

TABLE I (continued)

The Distribution of Bromine between Acetic Acid and Air

	B	G	Ratio
	0.12538	0.0002414	519.4
	0.12303	0.0002369	519.3
	0.11643	0.0002242	519.3
	0.10795	0.0002065	522.8
At 25°	0.10360	0.0002000	518.0
	0.09470	0.0001830	517.3
	0.09005	0.0001745	516.0
	0.08544	0.0001645	519.4
	0.08161	0.0001575	518.2
	0.06865	0.0001324	518.5
	0.04272	0.00008228	519.2
		Average	519.0
At 20°	0.58243	0.0009129	638.0
	0.28653	0.0004466	641.6
	0.22421	0.0003485	643.3
	0.17573	0.0002754	638.0
	0.13388	0.0002088	641.1
	0.11255	0.0001760	639.2
	0.10235	0.0001599	640.1
	0.09453	0.0001484	637.0
	0.08639	0.0001347	641.3
	0.07937	0.0001240	640.1
	0.07158	0.0001118	640.2
	0.05893	0.00009225	638.8
	0.04605	0.00007210	638.7
		Average	639.8
At 15°	0.59393	0.0007480	794.0
	0.35998	0.0004554	790.5
	0.19186	0.0002422	792.1
	0.13791	0.0001741	792.1
	0.12326	0.0001560	790.1
	0.10970	0.0001384	792.6
	0.10465	0.0001318	794.0
	0.09215	0.0001166	790.3
	0.08846	0.0001117	791.9
	0.07766	0.00009787	793.5
	0.05806	0.00007314	793.8
	0.04712	0.00005945	792.6
		Average	792.3

It is evident that this ratio is constant at any given temperature for all concentrations of bromine within the range of the experiments. The solu-

bility of bromine in acetic acid therefore follows Henry's law. This ratio is, therefore, a measure of the partial vapour pressure of bromine at different temperatures, and the temperature variation over the range in which the latent heat of vaporization is constant should be given by

$$\text{Log}_{10}R = \frac{Q}{4.6} \cdot \frac{1 + C}{T}.$$

It was found that between $15°$ and $40°C$.

$$\text{Log}_{10}R = \frac{1650}{T} - 2.828.$$

The values of R obtained by experiment agree fairly well with those calculated from this equation, as shown below.

Temperature °A	R (observed)	R (calculated)
288	792	796
293	640	636
298	519	513
303	419	415
313	277	278

The agreement between the values of R obtained by experiment and those obtained by calculation is fairly satisfactory. The latent heat of bromine in acetic acid solution, obtained from the above values, is 48 calories, a value which is not far from that of liquid bromine (45.6 calories).

In order to ascertain the effect due to the presence of an indifferent salt, i.e. one that does not combine with bromine to form a perhalogen compound, solutions of sodium acetate, disodium hydrogen phosphate and potassium acetate in acetic acid were employed in place of the pure acid. The sulphates and nitrates of sodium and potassium were also tried, but proved to be too insoluble in acetic acid to be of any value. The results obtained are given in Table II, where A is the concentration of the salt, B is the concentration of the bromine in the salt solution, and G is the concentration of the bromine in air. All concentrations are given in gramme molecules per litre.

It is evident from the figures given in Table II that the dissolved salt has no appreciable effect upon the distribution coefficient. The ratios given in Table I can, therefore, be used for the calculation of the dissociation constants of the perhalides examined.

The distribution of bromine between solutions of lithium chloride in acetic acid and air at $25°C$ was now determined. The concentration of the lithium chloride was varied from 0.09367 to 0.04152 gramme molecules per litre and the concentration of the bromine in the solution from 0.12354 to 0.08685 gramme molecules per litre. Although the perhalide formed in

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TABLE II

The Distribution of Bromine between a Solution of
a Salt in Acetic Acid and Air at 25°

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A	B	G	Ratio
Sodium acetate			
0.97760	0.16462	0.0003191	515.9
—	0.15938	0.0003070.	518.6
0.60128	0.17242	0.0003310	520.9
—	0.16803	0.0003246	517.7
0.48830	0.16786	0.0003234	519.2
—	0.16349	0.0003160	517.2
		Average 518.2	
Disodium hydrogen phosphate			
0.23550	0.10309	0.0001987	518.8
—	0.09991	0.0001925	519.0
—	0.09662	0.0001861	519.1
		Average 519.0	
Potassium acetate			
0.80212	0.11147	0.0002143	520.1
—	0.10684	0.0002061	518.4
0.51255	0.20694	0.0003990	518.7
—	0.20258	0.0003919	516.9
0.12814	0.15094	0.0002906	519.4
—	0.14700	0.0002836	518.3
		Average 518.6	

dilute aqueous solution is the tri-halide, it does not follow that this will also
be the case in acetic acid solution. Therefore, four dissociation constants
were calculated, according to the equilibrium

$$\text{LiCl} + m\text{Br}_2 \rightleftarrows \text{LiCl.Br}_{2m}, \quad (m = 1, 2, 3, 4).$$

The corresponding equilibrium constant is given by

$$K = \frac{\left\{ na - \dfrac{b - x}{m} \right\} x^m}{\dfrac{b - x}{m}}.$$

where the concentration of the free bromine (x) is found by multiplying the
observed concentration in air by the distribution coefficient. The results are
shown in Table III.

TABLE III

The Dissociation of Lithium Chloro-Perbromides at 25°

B	G	X	K_1	K_2	K_3	K_4
a = 0.09367 M − LiCl						
0.11163	0.0001706	0.08854	0.2707	0.05579	0.00775	0.000936
0.10870	0.0001662	0.08626	0.2661	0.05468	0.00740	0.000869
0.10585	0.0001613	0.08371	0.2705	0.05510	0.00721	0.000822
		Average	0.2691	0.05519	0.00745	0.000876
a = 0.07862 M − LiCl						
0.09072	0.0001416	0.07348	0.2616	0.04395	0.00503	0.000503
0.08879	0.0001393	0.07230	0.2681	0.04359	0.00502	0.000496
0.08685	0.0001361	0.07064	0.2720	0.04344	0.00478	0.000460
		Average	0.2672	0.04366	0.00494	0.000486
a = 0.05968 M − LiCl						
0.11188	0.0001850	0.09602	0.2653	0.06017	0.00910	0.00120
0.10983	0.0001813	0.09409	0.2625	0.05828	0.00864	0.00111
0.10732	0.0001776	0.09217	0.2709	0.05839	0.00847	0.00106
		Average	0.2662	0.05895	0.00874	0.00112
a = 0.04152 M − LiCl						
0.12354	0.0002146	0.11138	0.2689	0.08020	0.01278	0.00195
0.12056	0.0002091	0.10852	0.2657	0.06945	0.01196	0.00177
0.11749	0.0002040	0.10588	0.2672	0.06902	0.01154	0.00167
		Average	0.2673	0.07289	0.01209	0.00180

The values of K_2, K_3 and K_4 increase rapidly with increase in the concentration of the halogen, and as the concentration of the lithium chloride decreases these values fall to a minimum at a concentration of 0.07862 gramme molecules per litre, and then rise with further decrease in the concentration. On the other hand, the value of K_1 remains fairly constant, and is evidently unaffected by alterations in the concentration of either the bromine or the halide, within the limits of the experimental conditions. It is, therefore, obvious that the principal perhalide formed is the trihalide, $LiClBr_2$, and it was not considered necessary to calculate the values of K other than K_1 in the case of the remaining chloro-perbromides examined. In order to save space the remaining data for the chloro-perbromides are summarised in Table IV. The values quoted for K_1 are the mean of usually three experiments, and the variation in K_1 is shown in the last column.

TABLE IV

The Dissociation of Chloro-Perbromides at 25°

Substance	A molality	B molality			K₁	Range		
NaClBr₂	0.10050	0.1393	—	0.1456	0.262	0.261	—	0.263
″	0.00948	0.1193	—	0.1262	0.260	0.258	—	0.261
KClBr₂	0.02640	0.1302	—	0.1364	0.263	0.261	—	0.2675
″	0.02255	0.1411	—	0.1496	0.262	0.257	—	0.266
AlCl₃Br₆	0.01225	0.1317	—	0.1383	0.267	0.265	—	0.269
″	0.01008	0.1000	—	0.1071	0.271	0.264	—	0.276
HgCl₂Br₄	0.03794	0.14995	—	0.1584	3.4465	3.368	—	3.5475
″	0.01897	0.18785	—	0.1959	2.994	2.972	—	3.008
FeCl₃Br₆	0.02676	0.1675	—	0.1782	1.422	1.422	—	1.423
″	0.02674	0.1553	—	0.1625	1.419	1.411	—	1.424
″	0.01531	0.0812	—	0.0852	1.056	1.052	—	1.059
″	0.01482	0.0664	—	0.0708	1.022	0.994	—	1.0665
SnCl₄Br₈	0.05078	0.1824	—	0.1866	3.0835	3.070	—	3.097
″	0.02734	0.1557	—	0.1612	2.391	2.386	—	2.405
″	0.01102	0.1118	—	0.11705	1.749	1.692	—	1.777
SbCl₅Br₁₀	0.05120	0.1121	—	0.1177	3.159	3.138	—	3.190
″	0.02550	0.1060	—	0.1117	2.408	2.3945	—	2.417

It is evident that the chlorides of sodium, potassium and aluminium behave "normally," i.e. they give a value of the dissociation constant K which agrees with that given by lithium chloride, at any rate at the concentrations examined, which were the greatest that could be obtained owing to the low solubility of these chlorides in acetic acid. On the other hand, the chlorides of mercury, iron, tin and antimony all give values that are considerably higher than those given by the "normal" halides. The values of K given by ferric chloride are distinctly lower than those of the other abnormally behaving halides examined, though they are still considerably higher than the normal value. In each case the value of K increases with increase of concentration of the halide.

The distribution of bromine between solutions of potassium bromide in acetic acid and air at 25° was next determined. The concentration of the potassium bromide was varied from 0.04199 to 0.00840 gramme molecules per litre, and that of the bromine from 0.22371 to 0.08573 gramme molecules per litre. As in the case of lithium chloride, four dissociation constants were calculated, corresponding to

$$KBr + mBr_2 \rightleftharpoons KBr_{2m+1}, \quad (m = 1, 2, 3, 4).$$

The results are given in Table V.

TABLE V
The Dissociation of Potassium Perbromides at $25°$

B	G	X	K_1	K_2	K_3	K_4
a = 0.04199 M − KBr.						
0.11294	0.0001160	0.06020	−0.0119	0.00220	0.000307	0.0000291
0.11122	0.0001148	0.05958	−0.0111	0.00221	0.000305	0.0000284
0.09829	0.00009921	0.05149	−0.00529	0.00211	0.000231	0.0000182
0.09709	0.0001008	0.05232	−0.00325	0.00239	0.000260	0.0000206
0.09592	0.00009720	0.05045	−0.00386	0.00215	0.000227	0.0000174
		Average	−0.00708	0.00221	0.000266	0.0000227
a = 0.04170 M − KBr.						
0.22371	0.0002854	0.14813	−0.00664	0.00227	0.00213	0.000575
0.22000	0.0002790	0.14480	−0.00645	0.00228	0.00201	0.000540
0.21439	0.0002688	0.13951	−0.00618	0.00221	0.00182	0.000491
		Average	−0.00642	0.00225	0.00199	0.000535
a = 0.02359 M − KBr.						
0.09101	0.0001183	0.06140	−0.0125	0.00224	0.000322	0.0000311
0.08835	0.0001147	0.05953	−0.0108	0.00226	0.000307	0.0000285
0.08573	0.0001111	0.05766	−0.00912	0.00226	0.000291	0.0000261
		Average	−0.0108	0.00225	0.000307	0.0000286
a = 0.02100 M − KBr.						
0.15769	0.0002340	0.12145	−0.0511	0.00234	0.00132	0.000287
0.15495	0.0002284	0.11854	−0.0502	0.00216	0.00122	0.000258
0.15223	0.0002245	0.11652	−0.0480	0.00238	0.00121	0.000249
0.11320	0.0001568	0.08138	−0.0277	0.00212	0.000528	0.0000718
0.11112	0.0001540	0.07993	−0.0262	0.00221	0.000521	0.0000691
0.10873	0.0001476	0.07661	−0.0267	0.00181	0.000436	0.0000556
		Average	−0.0383	0.00217	0.000872	0.000165
a = 0.00840 M − KBr.						
0.15307	0.0002658	0.13795	−0.0613	0.00211	0.00175	0.000443
0.14902	0.0002582	0.13400	−0.0586	0.00210	0.00159	0.000386
		Average	−0.0599	0.00211	0.00167	0.000415

It is obvious that in the case of potassium bromide the values of K_1, K_3 and K_4 vary greatly. The values of K_1 are all negative, and decrease rapidly with increase of bromine concentration, whilst the values of K_3 and K_4 are positive, and increase under these circumstances. The variations in the concentration of the halide also appear to have an effect upon these values, but, as shown below, if the concentration of the bromine is kept constant, an increase in the concentration of the halide causes a corresponding increase in the value of K_1 and a decrease in the values of K_3 and K_4.

Concentration of Halide	Concentration of Br in solution	K_1	K_3	K_4
0.00840	0.15307	−0.0613	0.00175	0.000443
0.02100	0.15495	−0.0502	0.00122	0.000258
0.02100	0.11112	−0.0262	0.000521	0.0000691
0.04199	0.11122	−0.0111	0.000305	0.0000284

The value of K_2 is not appreciably affected by variations in the concentration of either the halide or the bromine, and remains fairly constant. It therefore appears that in the case of potassium bromide it is the pentabromide that is the principal product in solutions moderately dilute with respect to bromine, and not the trihalide, as in the case of the chloro-perbromides. The values of K_1, K_2 and K_3 were calculated in the case of all the other bromides examined. The bromides of sodium and aluminium were found to behave in the same manner as potassium bromide, the value of K_2 remaining unaffected by variations in the concentrations of either the halide or the bromine, whilst the values of K_1 and K_3 vary considerably, and in the same manner as in the case of the potassium salt. These halides are, therefore, "normal" salts. The bromides of cadmium, mercury and tin give abnormal values for K_1, K_2 and K_3. The data for the perbromides are summarised in Table VI. In order to save space the values of K_1 and K_3 are not shown, and the values quoted for K_2 are the mean of usually three experiments. The variation in K_2 is shown in the last column.

TABLE VI

The Dissociation of Perbromides at 25°

Substance	A molality	B molality		K_2	Range	
NaBr$_3$	0.02419	0.1905	− 0.1994	0.00226	0.00215	− 0.00233
''	0.00964	0.1478	− 0.15395	0.00228	0.00224	− 0.00234
AlBr$_9$	0.03271	0.1735	− 0.1759	0.00226	0.00226	− 0.00227
''	0.01478	0.1658	− 0.1710	0.00225	0.00223	− 0.00228
''	0.00773	0.1548	− 0.1602	0.00223	0.00219	− 0.00228
CdBr$_6$	0.02977	0.1306	− 0.1376	0.257	0.241	− 0.265
''	0.01488	0.1707	− 0.1788	0.1775	0.172	− 0.184
HgBr$_6$	0.038705	0.17075	− 0.1770	1.747	1.696	− 1.7915
''	0.038705	0.07875	− 0.0805	1.689	1.640	− 1.748
''	0.03413	0.1676	− 0.1762	1.561	1.5515	− 1.567
''	0.01935	0.0916	− 0.0962	1.280	1.2555	− 1.307
''	0.017065	0.1528	− 0.1567	1.194	1.187	− 1.201
SnBr$_{12}$	0.11558	0.1151	− 0.1211	0.437	0.433	− 0.441
''	0.04973	0.1229	− 0.1288	0.310	0.295	− 0.319
''	0.024865	0.1088	− 0.1148	0.200	0.193	− 0.206
''	0.01243	0.1376	− 0.1415	0.152	0.145	− 0.159

The dissociation constants of lithium chloro-perbromides and potassium perbromides in acetic acid solutions at various temperatures were now determined, the temperatures chosen being 40°, 30°, 20° and 15°. In each case four dissociation constants were calculated, corresponding to the four constants already calculated at 25°, the results obtained were similar to those found with these two compounds at the latter temperature. The data for lithium chloro-perbromide are summarised in Table VII, and those for potassium perbromide in Table VIII. The values of K_1 in the former case and of K_2 in the latter case are the mean of usually four experiments, The values of K_2, K_3 and K_4 for lithium chloro-perbromide and of K_1, K_3 and K_4 for potassium perbromide have been omitted.

TABLE VII

The Dissociation of Lithium Chloro-Perbromide at Different Temperatures

Temperature	A molality	B molality	K_1
40°	0.06581	0.09285 — 0.1065	0.266
30°	0.04396	0.0762 — 0.0832	0.268
20°	0.09367	0.1713 — 0.1856	0.268
20°	0.07545	0.1820 — 0.1885	0.266
15°	0.05540	0.1239 — 0.1289	0.268

TABLE VIII

The Dissociation of Potassium Perbromide at Different Temperatures

Temperature	A molality	B molality	K_2
40°	0.03299	0.1067 — 0.11775	0.00218
30°	0.02250	0.1167 — 0.1259	0.00216
20°	0.02090	0.1614 — 0.1696	0.00227
15°	0.02492	0.1328 — 0.1345	0.00223

It is evident from these results that the dissociation constant does not vary with the temperature within the range of the experiments, and that over the whole range of temperatures considered the chloro-perbromides exist principally as the tri-halides, whilst the perbromides exist mainly as penta-halides.

In order to compare the results obtained in acetic acid with those obtained in water, the dissociation constants of lithium chloro-perbromide and potassium perbromide in aqueous solution were now determined. As already stated, this determination was carried out by the method of Jakowkin. Determinations were made at 40°, 30°, 25°, 20° and 15°, but as satisfactory results had already been obtained with potassium perbromide at 25° it was not thought necessary to carry out any further experiments at this temperature with the latter compound. Before the values of K could be calculated it was

necessary to determine the distribution ratios of bromine between water and carbon tetrachloride at these temperatures, at any rate for a range of concentrations somewhat exceeding the limits of those employed in the determination of the dissociation constants. These distribution ratios are given in Table IX. The ratio at $25°$ was not determined, Jakowkin's figures being used instead. The data for lithium chloro-perbromide and potassium perbromide are summarised in Tables X and XI, the values quoted for K_1 being the mean of usually four experiments.

TABLE IX

The Distribution of Bromine between Water and Carbon Tetrachloride at Different Temperatures

	B	G	Ratio
At 40°	0.02088	0.67767	32.46
	0.01929	0.60117	31.16
	0.01602	0.50610	31.60
	0.01302	0.39840	30.61
	0.01120	0.34221	30.55
	0.01001	0.30066	30.05
	0.007601	0.22656	29.81
	0.006229	0.18650	29.94
	0.005820	0.17240	29.62
	0.004245	0.12278	28.92
	0.003455	0.10124	29.30
	0.002152	0.06287	29.22
	0.001920	0.05569	29.00
	0.001208	0.03514	29.15
	0.001060	0.03079	29.04
At 30°	0.02959	0.99282	33.56
	0.02385	0.75958	31.84
	0.02154	0.65194	30.27
	0.01972	0.60064	30.45
	0.01533	0.44849	29.26
	0.01313	0.38200	29.10
	0.01205	0.35117	29.15
	0.009427	0.27345	29.00
	0.007730	0.22070	28.55
	0.007251	0.20962	28.91
	0.005912	0.16860	28.52
	0.004533	0.12773	28.18
	0.003528	0.09826	27.85
	0.002626	0.07301	27.00
	0.002065	0.05786	28.02

TABLE IX (Continued)

The Distribution of Bromine between Water and Carbon Tetrachloride at
Different Temperatures

	B	G	Ratio
At 20°	0.02535	0.77206	30.45
	0.02320	0.68118	29.36
	0.01865	0.52807	28.32
	0.01301	0.35849	27.55
	0.008125	0.21687	26.69
	0.007845	0.20653	26.33
	0.006504	0.17344	26.67
	0.005258	0.13826	26.29
	0.005291	0.13766	26.02
	0.004202	0.11015	26.21
	0.003236	0.08486	26.22
At 15°	0.03580	1.12675	31.47
	0.03131	0.95247	30.42
	0.03018	0.81538	28.80
	0.02336	0.66542	28.49
	0.02196	0.60013	27.33
	0.02040	0.55512	27.21
	0.01922	0.51684	26.89
	0.01762	0.47580	27.00
	0.01595	0.44815	27.27
	0.01521	0.40880	26.88
	0.01219	0.32756	26.87
	0.01096	0.28768	26.26
	0.009911	0.26089	26.32

TABLE X

The Dissociation of LiClBr$_2$ in Aqueous Solution at Different Temperatures

Temperature	A molality	B molality	K_1
.40°	0.05458	0.003144 — 0.01053	0.7455
30°	0.06043	0.006391 — 0.01120	0.747
25°	0.10254	0.005280 — 0.01302	0.747
20°	0.08849	0.009785 — 0.02783	0.745
15°	0.09358	0.01124 — 0.02279	0.742
15°	0.08978	0.007046 — 0.01081	0.745

TABLE XI

The Dissociation of KBr$_3$ in Aqueous Solution at Different Temperatures

Temperature	A molality	B molality	K_1
40°	0.05001	0.005819 — 0.01909	0.06325
30°	0.04712	0.01030 — 0.02104	0.0632
20°	0.02036	0.003980 — 0.01213	0.0628
15°	0.06704	0.007610 — 0.02935	0.0630

Discussion of Results

The method of determining the dissociation constants of perhalides in non-aqueous solutions used in this research has been found to give satisfactory results. It is, therefore, a practical method, and can be used in other cases where it is desired to investigate complex molecules and ions in non-aqueous solutions by means of the distribution method. The method is, of course, limited to those substances which are sufficiently soluble in the liquid chosen, and also in air.

The results obtained for the distribution of bromine between water and carbon tetrachloride at different temperatures show that in each case the ratio increases as the concentration of the halogen is increased, and, therefore, agree with those obtained by Jakowkin at 25°. The curves obtained at the various temperatures are approximately parallel at the comparatively low concentrations investigated; thus indicating that at these concentrations the increase in the distribution ratio of bromine is approximately constant at all temperatures between 15° and 40°. The distribution of bromine between acetic acid and air does not show this increase, but remains constant with increase in the concentration of the bromine.

The values obtained for the dissociation constant of perhalides in acetic acid solution show that in the case of the chloro-perbromides the principal halide existing in the solution is the trihalide, as it is in the case of these compounds in aqueous solution. The results obtained with the perbromides, however, indicate that these compounds exist in acetic acid solution principally as pentabromides, whilst in aqueous solution, under similar conditions, they exist mainly as tribromides. Although the dissociation of periodides in acetic acid solution could not be determined by the method employed because of the low solubility of iodine in air, it appears probably that they, too, would be found to exist as penta- or higher perhalides in this solvent. The results obtained by Dawson and his co-workers[1] are not inconsistent with the view that in some organic solvents the perhalides tend to form compounds richer in halogen as we pass up the series from the chloro-perbromides to the periodides.

Where the same halides have been investigated in both aqueous and acetic acid solutions it has been found that those which give normal values of the dissociation constant in the one case also give normal values in the other, and those which give abnormal values in aqueous solution also give abnormal values in acetic acid. It is, therefore, probable that the other "normal" halides investigated in aqueous solution, but not in acetic acid, would also behave normally in this respect in the latter solvent; and that because aluminium perbromide has been found to give a normal value in acetic acid, it would also be found to give a normal value in aqueous solution. When the values of the dissociation constants obtained with the "normal" halides in aqueous and acetic acid solutions are compared, it is found that those ob-

[1] Loc. cit.

tained in the latter case are much smaller than those obtained in the former. Table XII shows the mean values of K_1 obtained with the chloro-perbromides at $25°$ in aqueous and acetic acid solutions.

TABLE XII

Mean Values of K_1 obtained with Chloro-Perbromides in Aqueous and Acetic Acid Solutions at $25°$

Salt	K_1 (aqueous)	K_1 (acetic acid)
$LiClBr_2$	0.75	0.267
$KClBr_2$	0.73 (Jakowkin)	0.263
$AlCl_3Br_6$	0.72	0.269

This difference in the value of K_1 indicates a smaller degree of dissociation of the perhalides in acetic acid than takes place in aqueous solution. In both aqueous and acetic acid solution the value of K given by the "normal" perhalides is found to be constant at temperatures ranging from $15°$ to $40°$. Jakowkin[1] found the value of K at $36.5°$ for KBr_3 to be 0.069, whilst the value at $25°$ for the same compound was only 0.063, and, therefore, concluded that the dissociation constant of the perhalides increases with increase of temperature. This is a result which might be expected, but it may be pointed out that the value of K at the higher temperature was not determined with anything approaching the accuracy of that at $25°$, and the differences between individual values obtained at the latter temperature are sometimes as great as that found between the values obtained at the two temperatures.

The dissociation constants of certain halides were found to have a much greater value than that given by "normal" compounds, whether the chloro-perbromides or the perbromides of the metals in question were chosen for investigation. The compounds of cadmium, mercury, iron, tin and antimony all showed this abnormal behaviour, which corresponds closely with that shown by the chloro-perbromides, perbromides and periodides of cadmium and mercury in aqueous solution. As in the case of the "normal" perhalides, the chloro-perbromides of these abnormally behaving metals evidently exist in acetic acid solution mainly as the trihalides, whilst the corresponding perbromides exist as the pentahalides. In each case the value of K increases considerably with increase in the concentration of the halide. The mercury salts show the greatest variation from the normal values. The only compounds which have shown this abnormal behaviour in aqueous solution are the perhalides of cadmium and mercury, but it is evident from the results obtained in this investigation that the number of "abnormal" compounds must be extended to ferric, stannic and antimonic perhalides, and it is probable that there are still others. The three new "abnormal" salts could not be examined in aqueous solution because they are not stable in water.

[1] Z. physik. Chem. 20, 19 (1896).

TABLE XIII

The "Active Fraction" of Abnormally Behaving Chlorides in Acetic Acid Solution at 25°

Chloride	$[\Sigma ClBr_2]$	$[Br_2]$	$[\Sigma Cl]$ calculated	$[\Sigma Cl]+[\Sigma ClBr_2]$	"Active fraction" %
Mercuric chloride, HgCl₂					
0.03794	0.00318	0.15518	0.00543	0.00861	11.34
	0.00325	0.15072	0.00571	0.00896	11.82
	0.00312	0.14683	0.00563	0.00875	11.53
0.01897	0.00232	0.19358	0.00317	0.00549	14.47
	0.00225	0.18964	0.00314	0.00539	14.21
	0.00221	0.18564	0.00315	0.00536	14.13
Ferric chloride, FeCl₃					
0.026760	0.00856	0.16966	0.01337	0.02193	27.32
	0.00836	0.16406	0.01350	0.02186	27.23
	0.00809	0.15944	0.01345	0.02154	27.83
0.026740	0.00783	0.15466	0.01342	0.02125	26.49
	0.00776	0.15113	0.01361	0.02137	26.64
	0.00756	0.14771	0.01356	0.02112	26.33
0.015309	0.00329	0.08190	0.01065	0.01394	30.35
	0.00317	0.07801	0.01077	0.01394	30.35
0.014820	0.00266	0.06814	0.01035	0.01301	29.26
	0.00277	0.06602	0.01112	0.01389	31.24
	0.00265	0.06373	0.01102	0.01367	30.75
Stannic chloride, SnCl₄					
0.050782	0.01099	0.17563	0.01659	0.02758	13.58
	0.01067	0.17169	0.01647	0.02714	13.36
0.027342	0.00662	0.15461	0.01135	0.01797	16.43
	0.00656	0.15191	0.01144	0.01800	16.46
	0.00644	0.14926	0.01143	0.01787	16.34
0.011020	0.00266	0.11439	0.00616	0.00882	20.01
	0.00261	0.11184	0.00618	0.00879	19.94
	0.00267	0.10909	0.00649	0.00916	20.78
Antimony chloride, SbCl₅					
0.051196	0.00860	0.10909	0.02089	0.02949	11.52
	0.00828	0.10665	0.02058	0.02886	11.27
	0.00818	0.10396	0.02085	0.02903	11.34
0.025502	0.00537	0.10629	0.01339	0.01876	14.71
	0.00528	0.10344	0.01353	0.01881	14.75
	0.00512	0.10090	0.01345	0.01857	14.57

TABLE XIV

The "Active Fraction" of Abnormally Behaving Bromides in Acetic Acid Solution at $25°$

Bromide	$[\Sigma Br_5]$	$[Br_2]^2$	$[\Sigma Br]$ calculated	$[\Sigma Br]+[\Sigma Br_5]$	Active fraction %
Cadmium bromide, $CdBr_2$					
0.02977	0.00360	0.021412	0.00038	0.00398	6.68
	0.00343	0.016194	0.00048	0.00391	6.57
	0.00354	0.015259	0.00052	0.00406	6.82
0.01488	0.00407	0.029119	0.00031	0.00438	14.72
	0.00413	0.027755	0.00033	0.00446	14.99
	0.00391	0.026545	0.00033	0.00424	14.25
Mercuric bromide, $HgBr_2$					
0.038705	0.00132	0.030424	0.00010	0.00142	1.83
	0.00125	0.029404	0.00010	0.00135	1.74
	0.00127	0.028296	0.00027	0.00154	1.99
0.038705	0.00030	0.006379	0.00011	0.00041	0.53
	0.00027	0.006117	0.00010	0.00037	0.48
0.034129	0.00131	0.030121	0.00010	0.00141	2.07
	0.00123	0.028716	0.00010	0.00133	1.95
	0.00117	0.027322	0.00010	0.00127	1.86
0.019350	0.00028	0.009149	0.00007	0.00035	0.90
	0.00025	0.008727	0.00006	0.00031	0.80
	0.00025	0.008295	0.00006	0.00031	0.80
0.017065	0.00068	0.024129	0.00006	0.00074	2.17
	0.00063	0.022952	0.00006	0.00069	2.02
Stannic bromide, $SnBr_4$					
0.115578	0.01046	0.010031	0.00235	0.01281	2.77
	0.00960	0.009189	0.00235	0.01195	2.59
0.049730	0.00818	0.012638	0.00146	0.00964	4.85
	0.00741	0.012358	0.00135	0.00876	4.40
	0.00716	0.011788	0.00137	0.00853	4.29
0.024865	0.00529	0.010862	0.00110	0.00639	6.42
	0.00481	0.010453	0.00104	0.00585	5.88
	0.00468	0.009898	0.00106	0.00574	5.77
0.012432	0.00527	0.017142	0.00069	0.00596	11.98
	0.00467	0.016461	0.00064	0.00531	10.68

Van Name and Brown[1] attribute the abnormal behaviour of the salts of cadmium and mercury towards the trihalide equilibrium to the power to unite with the halogen being limited to the normal molecules and ions, and have shown that if we accept this view we can calculate that portion of the total halide concentration which is in the form of simple molecules, which they call the "active fraction." If we make the reasonable assumption that

[1] Am. J. Sci., [iv], **44**, 105 (1917).

the abnormality shown by these halides in acetic acid solution may be attributed to the same reason as that shown by them in aqueous solution, we can calculate the "active fraction" in this case also. The chloro-perbromides exist in acetic acid solution as the trihalides; the calculation is, therefore, the same as in the case of the salts in aqueous solution, except that Br_2 is obtained by multiplying G by the distribution coefficient of bromine in the former case. The perbromides, however, exist as the pentahalides in acetic acid solution, and must be calculated from the equation.

$$K = \frac{[\Sigma Br] [Br_2]^2}{Br_5},$$

where $[\Sigma Br]$ and $[\Sigma Br_5]$ represent the total concentrations of the bromide and pentabromide radicles. Table XIII shows the "active fraction" of the abnormally behaving chloro-perbromides, and Table XIV shows those of the abnormally behaving perbromides.

Owing to the low solubility of cadmium and mercuric halides in acetic acid the results obtained are not so reliable as some of those obtained in aqueous solution. It is, however, obvious that in all the abnormal salts examined the magnitude of the "active fraction" decreases with the concentration of the halogen, and increases as the concentration of the halide is reduced. This result agrees with that found in aqueous solution, and is to be expected. It is also found that where the chloride and bromide of the same metal have been examined, e.g. in the case of mercury and tin, the magnitude of the "active fraction" is much larger in the case of the chloride than it is in that of the bromide. This again agrees with the results found in aqueous solution. In this case it was also found that the "active fraction" was greater in the case of the bromide than in that of the iodide. The magnitude of the "active fraction," therefore, decreases as the atomic weight of the halogen in combination with the metal increases. The value of the "active fraction" in pure solutions of the halides could not be calculated because a sufficient range of concentrations of bromine, expecially of very low concentrations, had not been investigated to enable this value to be obtained.

Summary

A modification of the distribution method of investigating the dissociation of the perhalides, in which the atmosphere in contact with the solvent takes the place of one of the liquids employed in the usual method, has been developed and utilized for the examination of the dissociation of chloro-perbromides and perbromides in glacial acetic acid. It has been found possible by means of this method to extend the investigation to a number of halides which cannot be examined in aqueous solution, e.g. the chlorides of iron, tin and antimony, and the bromide of tin.

It has been found that those halides which give a normal value of K in aqueous solution also give a normal value in acetic acid, but that the magnitude of K is much less in the latter case. It has also been shown that whilst

the chloro-perbromides exist principally as trihalides in both aqueous and acetic acid solution, the perbromides exist mainly as tribromides in aqueous solution, but as pentabromides in acetic acid. The list of "normal" perhalides investigated has been extended to aluminium bromide and lithium chloride, which had not been previously investigated.

The halides of cadmium and mercury, which give abnormal values of K in aqueous solution, also give abnormal values in acetic acid, and in addition to these, the chlorides of iron, tin and antimony, and the bromide of tin were also found to give abnormal values. In every case the value of K is much greater than the normal value, and it increases with the concentration of the halide.

The percentage of simple molecules and ions in acetic acid solutions of the abnormally behaving salts has been calculated by Van Name and Brown's method, and it has been found that this percentage decreases with decrease in the concentration of the halogen, and increases with decrease in the concentration of the halide. The percentage is greater in the case of the chlorides of these metals than in that of the bromides.

The values of K for "normal" halides have been determined in both aqueous and acetic acid solutions, at temperatures ranging from $15°$ to $40°$, and it has been found in both cases that there is no appreciable change in the magnitude of these values over the whole range of temperatures employed.

The author wishes to express his thanks to Dr. G. Senter and Dr. S. Sugden for their valuable advice and guidance throughout the work.

REMARKS CONCERNING THE PHASE RULE

BY PIERRE VAN RYSSELBERGHE

The purpose of this note is to call the attention of physical chemists to a beautifully simple and general formulation of the phase rule obtained by De Donder[1] in 1920. The characteristic feature of this formulation is that it replaces the quantity c of the classical expression

$$v = c + 2 - \varphi \qquad (1)$$

(v = variance of the system, φ = number of phases) which is rather vaguely and ambiguously defined as the "number of independent constituents" by the quantity C − r which is the difference between the "total number of constituents of the system" and the "number of distinct chemical reactions" which can take place among the constituents of the system. We write

$$v = C - r + 2 - \varphi \qquad (2)$$

We shall: 1) show, following De Donder's method, that this expression of the phase rule is a direct consequence of thermodynamics; 2) illustrate by means of a series of classical examples the superiority of expression (2) over expression (1) and show the straightforward way in which the variance can be determined by means of expression (2) in a system of any degree of complications; 3) show how expression (2) leads to a simple and precise solution of the problem consisting of determining the masses of the constituents in the various phases. It is interesting to mention that the identity

$$c = C - r \qquad (3)$$

does not appear in Gibbs' theory.[2]

Bakhuis Roozeboom[3] after a short discussion of the concept of independent constituents, concludes "that the number of (independent) constituents can be either larger or smaller than the number of elements; but that it can never be larger than the number of molecular species and is in many cases smaller."

Expression (3) replaces this qualitative statement by a precise definition.

I. *Proof of the rule* $v = C - r + 2 - \varphi$

The total number of variables of a system of φ phases and C constituents is $C\varphi + 2$: the concentrations of all the constituents in all the phases, pressure and temperature (supposed to be uniform throughout the system).

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[1] Th. De Donder: "Leçons de Thermodynamique et de Chimie physique," 125-139 (1920).

[2] J. W. Gibbs: Equilibrium of heterogeneous substances, "The Collected Works of J. W. Gibbs," I, pp. 55-100, particularly pp. 96-97.

[3] H. W. Bakhuis Roozeboom: "Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," 1, 21 (1901).

We have $(\varphi - 1)$ C necessary conditions between the partial molal free energies of the constituents in the φ phases. For constituent i we have the $(\varphi - 1)$ conditions:

$$\overline{F}_{i1} = \overline{F}_{i2} \; - - - - = \overline{F}_{i\varphi} \quad (i = 1, 2, - - - C) \tag{4}$$

There are C series of analogous relations.

In each phase the sum of the mol fractions of the C constituents must be equal to 1. Hence we have φ relations of the type

$$\sum_{i=1}^{i=C} x_{ia} = 1 \qquad (a = 1, 2, - - - - \varphi) \tag{5}$$

If r reactions can take place among the C constituents we have r chemical equations of the type

$$\sum_{i=1}^{i=C} n_{i\rho} M_i = 0 \qquad (\rho = 1, 2, - - - r) \tag{6}$$

in which $n_{i\rho}$ is the coefficient of the chemical symbol of constituent i in the reaction ρ ($n_{i\rho}$ may be positive, negative or zero), M_i is the chemical symbol of constituent i; it also represents the molecular mass of this constituent. At equilibrium, the total variation of the free energy of the system must be zero with respect to the occurrence of any of the r reactions. We have then the r conditions:

$$\sum_{i=1}^{i=C} F_i n_{i\rho} M_i = 0 \qquad (\rho = 1, 2, - - - r) \tag{7}$$

We recall that

$$F = \sum_{i=1}^{i=C} F_i \tag{8}$$

and that

$$\overline{F}_{ia} = M_i \frac{\partial F}{\partial m_{ia}} \tag{9}$$

in which m_{ia} is the mass of constituent i present in the phase a. Hence we have $(\varphi - 1)$ C relations of the type (4), φ relations of the type (5) and r relations of the type (7) between the C $\varphi + 2$ variables. The variance is then:

$$v = C \varphi + 2 - (\varphi - 1) C - \varphi - r = C - r + 2 - \varphi \tag{10}$$

For a more complete and detailed thermodynamical theory the reader is referred to De Donder[1]

II. *Examples*

A. *Case of purely physical transformations.*

In this case r = 0 and c = C. The forms (1) and (2) of the phase rule coincide.

[1] Loc. cit.

B. *Case of physical and chemical transformations.*
We shall examine successively a number of typical examples.
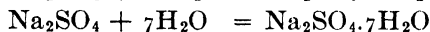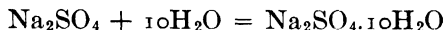1. *System $CaCO_3$, CaO, CO_2*
    The only reaction taking place under usual conditions is

$$CaCO_3 = CaO + CO_2$$

Hence $C = 3$, $r = 1$ and $c = C - r = 2$.

2. *System Na_2SO_4, H_2O, hydrates of Na_2SO_4.*
    Two hydrates are known. Hence two reactions take place:

$$Na_2SO_4 + 10H_2O = Na_2SO_4.10H_2O$$
$$Na_2SO_4 + 7H_2O = Na_2SO_4.7H_2O$$

We have: $C = 4$, $r = 2$, $c = C - r = 2$.
In the same way, we would find $c = 2$ for the system $FeCl_3$, H_2O or any other analogous system.

3. *System $Bi(NO_3)_3$, H_2O.*
    Four reactions take place:

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3$$
$$2Bi(NO_3)_3 + 3H_2O = Bi_2O(NO_3)_2(OH)_2 + 4HNO_3$$
$$Bi(NO_3)_3 + 5H_2O = Bi(NO_2)_3.5H_2O$$
$$Bi(NO_3)_3 + 1\tfrac{1}{2} H_2O = Bi(NO_3)_3.1\tfrac{1}{2}H_2O$$
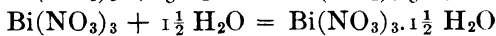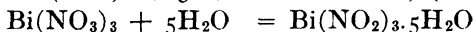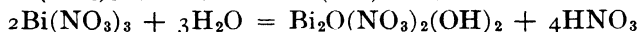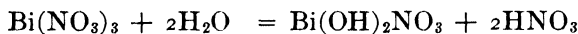
Hence: $C = 7$, $r = 4$, $c = C - r = 3$.

4. *System C, CO_2, CO, O_2.*
    The following reactions are known to occur

$$C + O_2 = CO_2$$
$$C + \tfrac{1}{2}O_2 = CO$$
$$CO + \tfrac{1}{2}O_2 = CO_2$$
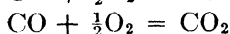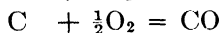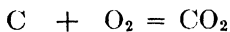
The first one, however, can be obtained by adding the other two.
Two of these three reactions are distinct.
Hence: $C = 4$, $r = 2$, $c = C - r = 2$.

5. *System H_2, O_2, H_2O.*
    The only reaction occurring is

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$
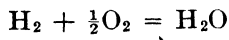
Hence $C = 3$, $r = 1$, $c = C - r = 2$.

6. *System Na_2SO_4, $MgSO_4$, H_2O.*
    In the case of stable equilibria the following reactions have to be considered:

$$Na_2SO_4 + 10H_2O = Na_2SO_4.10H_2O.$$
$$MgSO_4 + 7H_2O = MgSO_4.7H_2O.$$
$$Na_2SO_4 + MgSO_4 + 4H_2O = Na_2Mg(SO_4)_2.4H_2O.$$
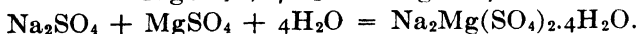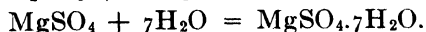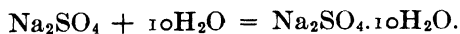
Hence: $C = 6$, $r = 3$, $c = C - r = 3$.

In the system carnallite, H_2O we would find:
$C = 9$ (H_2O, KCl, carnallite, $MgCl_2$, 5 hydrates of $MgCl_2$),
$r = 6$, $c = C - r = 3$.
In the system $FeCl_3$, HCl, H_2O we would find[1]
$C = 13$ (H_2O, $FeCl_3$, HCl, 4 hydrates of $FeCl_3$, 3 hydrates of HCl,
3 double hydrates of $FeCl_3$ and HCl), $r = 10$, $c = C - r = 3$.

7. *System Fe, CO, CO_2, C.*
The following reactions have to be considered:

$$Fe + CO = FeO + C$$
$$FeO + CO = Fe + CO_2$$
$$3FeO + CO_2 = Fe_3O_4 + CO$$
$$CO_2 + C = 2CO.$$
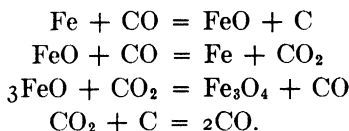
The last one can be deduced from a combination of the first two.
Hence $C = 6$, $r = 3$, $c = C - r = 3$.

8. *System Na_2SO_4, KCl, H_2O.*
The following reactions occur:
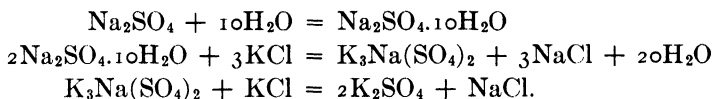
$$Na_2SO_4 + 10H_2O = Na_2SO_4.10H_2O$$
$$2Na_2SO_4.10H_2O + 3KCl = K_3Na(SO_4)_2 + 3NaCl + 20H_2O$$
$$K_3Na(SO_4)_2 + KCl = 2K_2SO_4 + NaCl.$$
Hence: $C = 7$, $r = 3$, $c = C - r = 4$.

III. *Determination of the masses of the constituents in the various phases of the system.*

De Donder[2] has solved this problem in a direct and unambiguous manner as we shall briefly show. The total number of variables includes now the masses of the φ phases. This total number is then $C\varphi + 2 + \varphi$. The masses of the individual constituents in each phase are deduced from the total mass of the phase and the corresponding mol fractions.

If the total masses of the $C - r$ "independent constituents" are given we have, besides the relations (4), (5) and (7) the $C - r$ conditions:

$$m_i = \sum_1^\varphi m_{ia} \quad (i = 1, 2, \ldots, C - r) \tag{11}$$

m_i being the total mass of constituent i and m_{ia} the mass of constituent i in the phase a. The variance is given by:

$$v' = C\varphi + 2 + \varphi - (\varphi - 1)C - \varphi - r - (C - r) \tag{12}$$

Or $\qquad v' = 2.$ $\hspace{6cm}$ (13)

[1] See A. Findlay: "The Phase Rule and its Applications."
[2] Loc. cit.

Conclusions

1. In the case of *purely physical transformations* (r = o), in order to determine the masses of all the phases it will be necessary to choose the masses of

2 phases when the system is invariant

1 phase when the system is monovariant

(the other arbitrarily chosen variable being then temperature, for instance). When the system has a variance larger than one, the problem can be entirely solved without knowing beforehand the mass of any of the phases, provided, of course, the total masses of the constituents are known. The arbitrarily chosen variables are then pressure and temperature.

2. In the case of *physical and chemical transformations* we give ourselves the total masses of the C − r "independent constituents." In order to determine the masses of all the constituents in the various phases it will be necessary to choose the masses of two, one or zero phases when the variance (v = C − r + 2 − φ) is zero, one or larger than one.

We see that the knowledge of the masses of the C − r "independent constituents" is not always sufficient to determine the masses of all the constituents in all the phases.

It is particularly in this respect that the formulation of the phase rule obtained by De Donder and its consequences are valuable. For further details the reader should consult De Donder's book.

Summary

The formulation of the phase rule obtained by De Donder involves a precise definition of the number of "independent constituents" of a heterogeneous system. Its application to systems of any degree of complication is simple and straightforward. It affords an unambiguous solution to the problem consisting of determining the masses of all the constituents in all the phases.

Stanford University,
California.

GRAVITATION CONSIDERED AS NEUTRAL MAGNETISM DUE TO MOTION OF ALL MATTER IN TIME

BY A. P. MATHEWS

The following theory that gravitation is neutral magnetism, set up by motion parallel to the time axis of space-time of all matter in our universe, has at least the merit of novelty, so far as I can find. In addition it enables the computation of the amount of gravitation of two hydrogen atoms, and also of the constant of gravitation, provided a certain velocity of motion in time be assumed. This assumed velocity is of the order of magnitude of the velocity in space of various stars, and is related in a very simple way to the velocity of light in space and also to the velocity in space of the negative end of the tube of force constituting the hydrogen atom. It is in fact equal to the velocity of the negative electron in its orbit in hydrogen of 2.187×10^8 cms/secs multiplied by $2/\sqrt{137.1}$; and 137.1 is the ratio of the velocity of light to 2.187×10^8 cms/secs.

While the proof that gravitation is neutral magnetism thus set up cannot be given until some independent determination of the velocity of movement of matter through space-time, or the ether, parallel with the time axis, at a rate of 3.736×10^7 cms/secs shall have been obtained, yet the simplicity of the idea and the not improbable velocity assumed is certainly in its favor. For the flow of time, i.e., of matter through space-time parallel with the time axis, is undoubted, being perceived both objectively in every time series of events and subjectively directly by consciousness, where it appears as the succession of states of consciousness; and the velocity of 3.736×10^7 cms/secs, or 232 miles per second, is less than the velocity in space recently ascribed by astronomers to distant island universes; that velocity being of the order of 10^9 cms/secs. It is of the order of magnitude of the motion of Betelgeuse, which is about 80 miles per second. There is, therefore, nothing improbable in the assumption as to the rate of motion in time.

All matter, so far as known, is moving in time with an unknown velocity, v_t, and is composed of hydrogen atoms. Most of these hydrogen atoms have been condensed to make more complex atoms. Each hydrogen atom, condensed and uncondensed, is an electrical di-pole, and so may be considered to be a unit of neutral, material electricity. Thus each mass of matter in the universe is a current of neutral electricity. All such currents are flowing in the same direction, in paths parallel to the time axis, and they are abreast in time. Such currents of ordinary electricity are known to attract each other if they be of the same sign. All neutral currents are of the same sign. Such neutral currents are known to attract each other. The attraction may be regarded as neutral magnetism. It is called gravitation.

Since each hydrogen atom consists of two electrons, one positive and one negative, each carrying 4.774×10^{-10} electrostatic units of positive or negative charge, we may regard these electrons as half units of neutral electricity, so that each hydrogen atom is, or carries, 4.774×10^{-10} electrostatic units of neutral, material electricity.

The translational motion of a charge, whether positive or negative, in space-time produces magnetism. The magnetism is polar, or dissymmetrical, if the two ends of the neutral charge or tube of force, the positive and negative charges, move in space at different rates; as, for example, when the negative moves about the positive in a hydrogen atom, or when the negative flows along a wire; but it is non-polar, or symmetrical, or neutral, if the two ends of the tube of force connecting the positive and negative electrons move at the same rate. Movement of a hydrogen atom as a whole in space does not set up ordinary, or polar, magnetism; but it must set up magnetism of some kind, since all motion of a charge, whether positive or negative, is known to set up magnetism. It is the peculiarity of gravitation that it is a neutral force. It is non-polar. It is neither positive nor negative, as is electrostatic force; nor is it north and south, as is ordinary magnetism.

The force of polar magnetism between two poles, north and south, or between two parallel currents of ordinary (positive or negative) electricity, is dependent upon the magnetic polarity of any material substance interposed between the poles or currents. It depends upon the magnetic permeability, μ, of that material. Non-polar, or neutral magnetism, would not, presumably, be at all affected by the interposition of matter; so far, at least, as either the magnetic or electrical polarity of that interposed matter is concerned. Corresponding with this expectation, gravitation is known to be independent both of the magnetic permeability and the specific inductive capacity of any matter interposed between gravitating masses.

Now if each condensed hydrogen atom, making a part of other atoms and carrying 4.774×10^{-10} electrostatic units of neutral electricity, by its motion in space generates neutral magnetism in the same manner and to the same degree as an equal quantity of negative or positive electricity, two hydrogen atoms of neutral charge, e, moving in parallel paths, abreast, and at a velocity of v_s in space, at a distance, d, apart, would act upon each other magnetically (attract) with a force expressed by the formula:

(1) $$\mu e^2/d^2 \times v_s^2 \text{ dynes},$$

when e is expressed in electromagnetic units; d in centimeters; and v_s, the velocity parallel to a space axis, in cms/secs.

Expressing this in electrostatic units we have:

(2) $$e^2/Kd^2 \times 1^2/c^2 \times v_s^2/1^2 \text{ dynes}.$$

In formula (2) the numeral, one, represents unit velocity; i.e., one centimeter per second.

Two hydrogen atoms moving abreast in parallel paths in space with unit velocity at unit distance and in the same direction should, therefore, if this

formula be correct, attract each other with the same magnetic force as two electrons[1] similarly moving, a force of $(4.774 \times 10^{-10})^2/(3 \times 10^{10})^2$ dynes, or $2.28 \times 10^{-19}/(9 \times 10^{20})$, or 2.533×10^{-40} dynes. And if they move in space in parallel paths with a velocity, c, that of light, then such atoms would attract with a force of 2.28×10^{-19} dynes, at unit distance, provided that this formula holds at such extreme velocities.

It hardly seems possible that the gravitational force between two hydrogen atoms due to their parallel motion in space can be as large as this. But on the other hand it is known that the mass of an electron does increase with the velocity of space motion, and directly as $c/\sqrt{(c^2 - v^2)}$; and also by the Newtonian law the gravitational force is a function of the mass. So that it is not improbable that the gravitational force would vary with space velocity as this formula states. If the mass increase with the velocity in the manner supposed by relativity, then formula (2) would need a correction which becomes of material importance only when the velocity comes very close to that of light, since the mass is supposed to become infinite at that velocity. The correction would be of the form $1/(1 - v^2/c^2)$. So that the corrected formula should be:

$$(3) \qquad e^2/Kd^2 \times 1^2/c^2 \times v_s^2/1^2 \times c^2/(c^2 - v_s^2);$$

$$\text{or, (4)} \qquad e^2/Kd^2 \times v_s^2/(c^2 - v_s^2) \text{ dynes.}$$

Whether gravitational attraction does vary with the velocity in space according to this formula, I do not know; but the corresponding formula for the velocity in time appears to give the correct result. Of course movement in space can hardly be the cause of gravitation as we know it since the various masses of matter are moving in all directions in space. But in time they are all moving at the same rate, in the same direction, in parallel paths.

The formula will be changed in one particular if the velocity of motion be not motion in space but motion in time. It is obvious, since a velocity is the ratio of the number of units of space extension traversed by the moving body to the number of units of time endured, that if we increase the component of the velocity parallel with the time axis we accomplish the same result as if we retarded the velocity of motion parallel with the space axis. Any increase in speed of motion parallel with the time axis appears to retard the velocity in space; and any decrease in motion parallel with the time axis appears to accelerate the motion in space; and vice versa, velocity in time appears to increase when velocity in space is diminished. This being so the force must vary inversely with the square of the time velocity, if it vary directly with the square of the space velocity. The mass of a body must be an inverse function of the velocity of its movement in time, if it be a direct function of its velocity in space.

Expressing, now, formula (2) in terms of time velocity, v_t, we have:

$$(5) \qquad e^2/Kd^2 \times 1^2/c^2 \times 1^2/v_t^2 \text{ dynes.}$$

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[1] Of course the electrostatic force of repulsion between two electrons overbalances this magnetic force; but such repulsion is absent between neutral charges.

Since the polar force of attraction of magnetism, the ordinary form, varies directly as the square of velocity in space it must be inversely as the square of the velocity in time. And if gravitation be neutral magnetism set up by the symmetrical motion in time of the tube of force, which is the atom, then gravitation must follow this same law. If it were corrected for the variation of mass with velocity we would have as the corrected formula:

(6) $\qquad e^2/Kd^2 \times 1^2/c^2 \times 1^2/v_t^2 \times (c^2 - v_t^2)/c^2$ dynes; or,

(7) $\qquad e^2/Kd^2 \times (c^2 - v_t^2)/c^4 v_t^2 \times 1^4$ dynes.

If we suppose that the velocity of the flow of time through matter in our universe, or the velocity of motion of matter parallel to a time axis of space-time, be at the same rate as the velocity of the negative electron moving in space about the positive center in the hydrogen atom, in Bohr's first orbit, or 2.187×10^8 cms/secs, this formula would give for the gravitational attraction of two condensed hydrogen atoms (atomic weight unity) at one centimeter distance $(4.774 \times 10^{-10})^2/(3 \times 10^{10} \times 2.187 \times 10^8)^2$ or 5.295×10^{-57} dynes.

This result is not far from being correct. In fact it is precisely $4/137.1$ times the correct figure. For since two one gram masses of matter more complex than hydrogen atoms at unit distance attract gravitationally with the force of 6.670×10^{-8} dynes, according to Heyl's recent careful determination, and there are, in a mass of one gram of material composed of atoms more complex than hydrogen, 6.061×10^{23} condensed hydrogen atoms, each pair of such atoms of hydrogen must attract at unit distance with the force of $6.670 \times 10^{-8}/(6.061 \times 10^{23})^2$ dynes. This is 1.815×10^{-55} dynes. This is $137.1/4$ times 5.295×10^{-57} dynes which the formula gives when assuming the motion to be 2.187×10^8 cms/secs.

It is clear from this that gravitation may be regarded as neutral magnetism set up by the translational motion of all matter parallel with the time axis. It is neutral because both ends of the tube of force are moving with the same velocity in time. The positive electron in the atom is moving in time at the same velocity as the negative. From formula (5) we may calculate what that velocity is. It is 3.736×10^7 cms/secs. This gives an exact result. This velocity is $(2.187 \times 10^8)/(\sqrt{137.1}/2)$. And 137.1 is $(3 \times 10^{10})/2.187 \times 10^8$. It is also 135×1.00776^2.

We may secure further evidence that this is correct. I have shown elsewhere how easily a hydrogen atom may be regarded as a very short light pulse which has been absorbed by the ether, becoming thus protohydrogen, and afterwards partly dissociated to form hydrogen by the absorption of a second pulse having twice the frequency of a Rydberg pulse. The first, or creative, light pulse, of a wave length of about 1.75×10^{-14} cms, is supposed to be moving parallel with the time axis. As long as it moves with the velocity of light it has $hc/2\pi$ erg-centimeters in it. This is the quantity, then, of the pulse before absorption. The gravitational attraction of two pulses thus moving in time with velocity of light will be zero, according to formula (7).

But if the pulses be reduced in velocity by absorption then they will attract each other. And at a distance of L between them, when moving with a velocity, v_t, or 2.187×10^8 cms/secs, the formula:

(8) $hc/2\pi L^2 \times 1^4/4c^2v_t^2$ dynes

gives, at 1 centimeter for L, the correct force of attraction of 1.815×10^{-55} dynes. Here again 1^4 represents unit velocity to the fourth power.

If, however, we consider the amount of erg-centimeters after absorption, in the atom itself, to be $hv'_s/2\pi$, where v'_s is the velocity of the negative electron in space, or 2.187×10^8 cms/secs, then the formula $hv'_s/2\pi L^2 \times 1^4/c^2v_t^2$ gives the correct value of 1.815×10^{-55} dynes for the attraction of the two atoms at unit distance, when v_t, the velocity in time, is 3.736×10^7 cms/secs, the value already found; h is 6.547×10^{-27} erg-secs, and c is 3×10^{10} cms/secs; L is of course unity. This is the same formula as (5) since $hv'_s/2\pi$ is precisely equal to e^2/K.

The gravitational attraction of two one-gram masses at a distance, d, apart, where the neutral charge, e, on each hydrogen atom is 4.774×10^{-10} e.s.u. will be:

(9) $(6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4/c^2v_t^2$ dynes.

And for any two masses of n and n' grams respectively it will be:

(10) $nn' (6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4/c^2v_t^2$ dynes.

This is the Newtonian law of gravitation; since $(6.061 \times 10^{23})^2 \times e^2/K \times 1^4/c^2v_t^2$ is the numerical value of the gravitational constant, k.

If it be corrected, as in formula (7) for velocities approaching the velocity of light, it would be, more correctly,:

(11) $nn' (6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4(c^2 - v_t^2)/c^4v_t^2$ dynes.

The velocity is of course the velocity in time rather than in space.

Since formula (7) gives the gravitational attraction of two condensed hydrogen atoms in other terms than $MM'k/d^2$, we may easily find the value of the gravitational constant, k, of the Newtonian law. If $m_{H'}$ is the mass of a condensed hydrogen atom and equal to $1.663 \times 10^{-24}/1.00776$ grams, the value of k will be:

(12) $k = e^2/Km^2_{H'} \times 1^4/c^2v_t^2$ dynes^{-1} velocity^4

$= (4.774 \times 10^{-10})^2 \times 1.00776^2/(1.663 \times 10^{-24} \times 3 \times 10^{10}$
                  $\times 3.736 \times 10^7)^2$

$= 6.670 \times 10^{-7}$ dynes^{-1} vel^4 $= 6.670 \times 10^{-8} (L^3)/(MT^2)$

We may conclude from this examination of the problem that gravitation may very well be a non-polar, or neutral, magnetic force, set up by the equal motion of both poles of the electric tubes of force constituting all matter. The motion is parallel with the time axis, so that all masses of matter con-

stitute parallel currents of neutral electricity; and the velocity of such movement of matter in our universe is at the rate of 3.736×10^7 cms/secs. This velocity may not be the same in other universes. If it vary from this figure the mass of the hydrogen atom and all other atoms would vary also somewhat and presumably the spectral lines of such atoms would be shifted slightly from their position as known to us.

Since motion in space seems to have the opposite effect to motion in time, producing energy in place of inertia, it may very well be that all matter repels other matter gravitationally in time, just as it appears to attract it in space. Accordingly all matter would appear to tend to distribute itself uniformly in time; while it tends to aggregate in space. So far as we know at present, matter is distributed, on the whole, uniformly in time, there being neither increase nor decrease in the total quantity of matter as time progresses.

University of Cincinnati.

ON THE HISTORY AND ANALYTICAL EXPRESSION OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS, AND THE RÔLE OF THE DIFFERENTIALS, dW AND dQ

BY GEORGE TUNELL

The fundamental physical facts on which the science of thermodynamics rests were established long ago. According to Gibbs thermodynamics as a science was brought into existence by Clausius. Gibbs[1] has summarized this part of the history of the subject in the following notable paragraphs:

"The fundamental questions concerning the relation of heat to mechanical effect, which had been raised by Rumford, Carnot, and others, to meet with little response, were now[2] everywhere pressing to the front.

" 'For more than twelve years,' said Regnault in 1853, 'I have been engaged in collecting the materials for the solution of this question:—Given a certain quantity of heat, what is, theoretically, the amount of mechanical effect which can be obtained by applying the heat to evaporation, or the expansion of elastic fluids, in the various circumstances which can be realised in practice?' The twenty-first volume of the Memoirs of the Academy of Paris, describing the first part of the magnificent series of researches which the liberality of the French government enabled him to carry out for the solution of this question, was published in 1847. In the same year appeared Helmholtz's celebrated memoir, 'Ueber die Erhaltung der Kraft.' For some years Joule had been making those experiments which were to associate his name with one of the fundamental laws of thermodynamics and one of the principal constants of nature. In 1849 he made that determination of the mechanical equivalent of heat by the stirring of water which for nearly thirty years remained the unquestioned standard. In 1848 and 1849 Sir William Thomson was engaged in developing the consequences of Carnot's theory of the motive power of heat, while Professor James Thomson in demonstrating the effect of pressure on the freezing point of water by a Carnot's cycle, showed the flexibility and the fruitfulness of a mode of demonstration which was to become canonical in thermodynamics. Meantime Rankine was attacking the problem in his own way, with one of those marvellous creations of the imagination of which it is so difficult to estimate the precise value.

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[1] "The Collected Works of J. Willard Gibbs," **2**, part 2, pp. 261, 262 (1928); or Proc. Am. Acad., New Series, **16**, 458, 459 (1889).

The history of the first and second laws has been stated by Lord Kelvin in different words but with very similar conclusions. Lord Kelvin's statement is given as an Appendix to this paper.

[2] In the eighteen-forties. (G.T.)

"Such was the state of the question when Clausius published his first memoir on thermodynamics: 'Ueber die bewegende Kraft der Wärme, und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen.'[3]

"This memoir marks an epoch in the history of physics. If we say, in the words used by Maxwell some years ago, that thermodynamics is 'a science with secure foundations, clear definitions, and distinct boundaries,' and ask when those foundations were laid, those definitions fixed, and those boundaries traced, there can be but one answer. Certainly not before the publication of that memoir. The materials indeed existed for such a science, as Clausius showed by constructing it from such materials, substantially, as had for years been the common property of physicists. But truth and error were in a confusing state of mixture. Neither in France, nor in Germany, nor in Great Britain, can we find the answer to the question quoted from Regnault. The case was worse than this, for wrong answers were confidently urged by the highest authorities. That question was completely answered, on its theoretical side, in the memoir of Clausius, and the science of thermodynamics came into existence. And as Maxwell said in 1878, so it might have been said at any time since the publication of that memoir, that the foundations of the science were secure, its definitions clear, and its boundaries distinct."

Unfortunately in the formulations of the fundamental principles given in the current text-books full use is not made of the symbols, forms, and theorems in the theory of functions of real variables best adapted to the problems at issue. These symbols and forms are essentially those of Clausius, and it is the purpose of this paper to point out this close relationship.

Clausius used several mathematical theorems the proofs of which he did not introduce into his texts. No proofs of these theorems will be given in this paper but the theorems will be stated and the reader will be referred to clear and rigorous proofs in the literature of the theory of functions of real variables.

The first law of thermodynamics was stated by Clausius[4] as follows:

"Die ganze mechanische Wärmetheorie beruht auf zwei Hauptsätzen. . . . Um den ersten Satz analytisch auszudrücken, denken wir uns irgend einen Körper, welcher seinen Zustand ändert, und betrachten die Wärmemenge, welche ihm während dieser Zustandsänderung mitgetheilt werden muss. Bezeichnen wir diese Wärmemenge mit Q, wobei eine vom Körper abgegebene Wärmemenge als aufgenommene negative Wärmemenge gerechnet werden soll, so gilt für das einer unendlich kleinen Zustandsänderung entsprechende Element dQ der aufgenommenen Wärme folgende Gleichung:

(I.) $$dQ = dU + AdW.$$

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[3] Read in the Berlin Academy, February 18, 1850, and published in the March and April numbers of Poggendorff's "Annalen."

[4] "Abhandlungen über die mechanische Wärmetheorie," Zweite Abtheilung, Abhandlung IX (1867).

The quotations in German may be skipped without disruption of the consecutive development of the subject matter although it is believed that the statements of Clausius are of no inconsiderable interest to the student of thermodynamics.

Hierin bedeutet U die Grösse, welche ich zuerst in meiner Abhandlung von 1850 in die Wärmelehre eingeführt und als die Summe der hinzugekommenen freien Wärme und der zu innerer Arbeit verbrauchten Wärme definirt habe. W. Thomson hat für diese Grösse später den Namen *Energie* des Körpers vorgeschlagen, welcher Benennungsweise ich mich, als einer sehr zweckmässig gewählten, angeschlossen habe, wobei ich aber doch glaube, dass man sich vorbehalten kann, in solchen Fällen, wo die beiden in U enthaltenen Bestandtheile einzeln angedeutet werden müssen, auch den Ausdruck *Wärmeund Werkinhalt* zu gebrauchen, welcher meine ursprüngliche Definition in etwas vereinfachter Form wiedergibt. W bedeutet die während der Zustandsänderung des Körpers gethane äussere Arbeit, und A das Wärmeäquivalent für die Einheit der Arbeit oder kürzer *das calorische Aequivalent der Arbeit.* Hiernach ist AW die nach Wärmemaasse gemessene äussere Arbeit oder, gemäss einer kürzlich von mir vorgeschlagenen bequemeren Benennungsweise, das äussere *Werk.*

"Wenn man der Kürze wegen das äussere Werk durch einen einfachen Buchstaben bezeichnet, indem man setzt:

$$AW = w,$$

so kann man die vorige Gleichung folgendermaassen schreiben:

(Ia.) $dQ = dU + dw$."

Clausius continued farther on:

"[Eine Grösse], welche sich auf den ersten Hauptsatz bezieht, ist die schon im Anfange dieser Abhandlung besprochene, in Gleichung (Ia.) enthaltene Grösse U, welche den Wärme- und Werkinhalt oder die Energie des Körpers darstellt. Zur Bestimmung dieser Grösse ist die Gleichung (Ia.) anzuwenden, welche wir so schreiben können:

(57) $dU = dQ - dw,$

oder, wenn wir sie uns integrirt denken:

(58) $U = U_0 + Q - w.$

Hierin stellt U_0 den Werth der Energie für einen willkürlich gewählten Anfangszustand des Körpers dar, und Q und w bedeuten die Wärmemenge, welche man dem Körper mittheilen muss, und das äussere Werk, welches gethan wird, während der Körper auf irgend eine Weise aus jenem Anfangszustande in den gegenwärtigen Zustand übergeht. . . ."

From the preceding paragraphs Clausius obtained an important conclusion, his equation (5), by the following reasoning:

"Wenn die Grössen x und y den Zustand des Körpers bestimmen, so muss die Grösse U, die Energie des Körpers, welche nur von dem augenblicklich stattfindenden Zustande des Körpers abhängt, sich durch eine Function dieser beiden Veränderlichen darstellen lassen.

"Anders verhält es sich mit den Grössen w and Q. Die Differentialcoëfficienten dieser Grössen, welche wir folgendermaassen bezeichnen wollen:

(1)
$$\frac{dw}{dx} = m \; ; \; \frac{dw}{dy} = n$$

(2)
$$\frac{dQ}{dx} = M \; ; \; \frac{dQ}{dy} = N,$$

sind bestimmte Functionen von x und y. Wenn nämlich festgesetzt wird, dass die Veränderliche x in x + dx übergehen soll, während y unverändert bleibt, und dass diese Zustandsänderung des Körpers in umkehrbarer Weise geschehen soll, so handelt es sich um einen vollkommen bestimmten Vorgang, und es muss daher auch das dabei gethane äussere Werk ein bestimmtes sein, woraus weiter folgt, dass der Bruch dw/dx ebenfalls einen bestimmten Werth haben muss. Ebenso verhält es sich, wenn festgesetzt wird, dass y in y + dy übergehen soll, während x constant bleibt. Wenn hiernach die Differentialcoëfficienten des äusseren Werkes w bestimmte Functionen von x und y sind, so muss zufolge der Gleichung (Ia.) auch von den Differential-coëfficienten der vom Körper aufgenommenen Wärme Q dasselbe gelten, dass auch sie bestimmte Functionen von x und y sind.

"Bilden wir nun aber für dw und dQ ihre Ausdrücke in dx und dy, indem wir unter Vernachlässigung der Gleider, welche in Bezug auf dx und dy von höherer Ordnung sind, schreiben:

(3)
$$dw = mdx + ndy$$

(4)
$$dQ = Mdx + Ndy,$$

so erhalten wir dadurch zwei vollständige Differentialgleichungen, welche sich nicht integriren lassen, so lange die Veränderlichen x und y von einander unabhängig sind, indem die Grössen m, n und M, N der Bedingungsgleichung der Integrabilität, nämlich:

$$\frac{dm}{dy} = \frac{dn}{dx} \; \text{resp.} \; \frac{dM}{dy} = \frac{dN}{dx},$$

nicht genügen. Die Grössen w und Q gehören also zu denjenigen, ... deren Eigenthümlichkeit darin besteht, dass zwar ihre Differentialcoëffi-cienten bestimmte Functionen der beiden unabhängigen Veränderlichen sind, dass *sie selbst aber nicht durch solche Functionen dargestellt werden können sondern sich erst dann bestimmen lassen, wenn noch eine weitere Beziehung zwischen den Veränderlichen gegeben und dadurch der Weg der Veränderungen vorgeschrieben ist.*"[5] (Italics in the last sentence by the author of this paper.)

"Kehren wir nun zur Gleichung (Ia.) zurück und setzen darin für dw und dQ die Ausdrücke (3) und (4) und zerlegen ebenso dU in seine beiden auf dx und dy bezüglichen Theile, so lautet die Gleichung:

$$Mdx + Ndy = \left(\frac{dU}{dx} + m\right) dx + \left(\frac{dU}{dy} + n\right) dy.$$

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[5] The importance of this sentence makes it worth while to offer the following translation: The quantities w and Q belong to those quantities. . . . the peculiarity of which is that, while their differential coefficients are definite functions of the two independent variables (x and y), the quantities themselves cannot be represented by such functions and can only then be determined when a further relation is given between the variables and the path of the changes is thereby prescribed.

Da diese Gleichung für alle beliebigen Werthe von dx und dy gültig sein muss, so zerfällt sie in folgende zwei:

$$M = \frac{dU}{dx} + m$$

$$N = \frac{dU}{dy} + n.$$

Differentiiren wir die erste dieser Gleichungen nach y und die zweite nach x, so erhalten wir

$$\frac{dM}{dy} = \frac{d^2U}{dxdy} + \frac{dm}{dy}$$

$$\frac{dN}{dx} = \frac{d^2U}{dydx} + \frac{dn}{dx}.$$

Nun ist auf U der für jede Function von zwei unabhängigen Veränderlichen geltende Satz anzuwenden, dass, wenn man sie nach den beiden Veränderlichen differentiirt, die Ordnung der Differentiationen gleichgültig ist, so dass man setzen kann:

$$\frac{d^2U}{dxdy} = \frac{d^2U}{dydx}.$$

Wenn man unter Berücksichtigung dieser letzten Gleichung die zweite der beiden vorigen Gleichungen von der ersten abzieht, so kommt:

(5) $$\frac{dM}{dy} - \frac{dN}{dx} = \frac{dm}{dy} - \frac{dn}{dx}.\text{''}$$

The attempt will next be made to prove that the essentials of Clausius's analytical expressions of the first law are in accord with the theory of functions of real variables; Planck's objection to Clausius's use of dQ and its designation as a differential is based on an argument that will be proved erroneous.

The simplest system discussed in thermodynamics consists of a fixed quantity, for example one gram or one mol, of one gaseous phase containing only one component, throughout which the temperature and pressure are uniform. For such a system there exists a characteristic relation that may be expressed as follows:

(1) $$\Phi(p,v,t) = 0,\text{[6]}$$

where p denotes the pressure; v, the volume; and t, the temperature of the gas on the scale of the constant volume hydrogen thermometer, which has been adopted as standard by the International Bureau of Weights and Measures (at Sèvres, France). On the centigrade scale of this thermometer the temperature of melting ice is taken as 0° and that of the vapor of distilled

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[6] The present discussion applies to systems such as steam, a satisfactory representation of which is not given by a simple, highly specialized equation of state such as the perfect gas law or van der Waals's equation.

water boiling under normal atmospheric pressure as 100°, the hydrogen being under a pressure of one meter of mercury when the temperature is 0°.

The characteristic equation of the gas is in general such that by means of it any one of the variables can be represented as a function of the other two.

For reversible processes (continuous series of equilibrium states)[7] the work done by the system (work of the path),[8] W, is defined by the equation

$$(2) \qquad W = \int_{(t_o,p_o)}^{(t,p)} pdv = \int_{(t_o,p_o)}^{(t,p)} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp,$$

where W is measured in mechanical units. The heat received (heat of the path), Q, is defined by the equation

$$(3) \qquad Q = \int_{(t_o,p_o)}^{(t,p)} c_p dt + l_p dp,$$

where c_p and l_p denote some functions of t and p, and Q is measured in thermal units. These definitions correspond to the facts stated by Clausius that the work done and the heat received each depends on all of the intermediate states as well as the initial and final states; the integrals in (2) and (3) are line integrals that depend on the particular choice of the path of integration. As Clausius says, the quantities W and Q can only be determined when an additional relation between the variables that determine the state of the system is given and the path of the changes is thereby fixed.

The justification for the introduction of heat as a physical quantity in thermodynamics (as contrasted with the justification for the definition utilized in kinetic theory) is well stated by Preston[9] as follows:

"In order to account for the sensation experienced in presence of a hot body an active agent is postulated, and the name given to this agent is heat. A hot body is regarded as a source of heat just as a luminous body is regarded as a source of light. In the same way, when two bodies at different temperatures are placed in contact, the temperature of the warmer falls while that of the other rises. To account for this we say that *heat* passes from one to the other, that the warmer loses heat and the colder gains it. In this sense heat is regarded as something which may be added to or taken away from matter;

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[7] "On dit qu'une transformation est opérée par voie réversible quand elle est constituée par une succession d'états d'equilibre. Une transformation ne peut donc se produire réelement par voie rigoureusement réversible; elle est la limite de deux séries de transformations réalisables et s'effectuant en sens inverses." H. Bouasse: "Cours de Thermodynamique," Deuxième édition, Première partie, 70 (1913).

[8] Gibbs says: "Suppose the body to change its state, the points associated with the states through which the body passes will form a line, which we may call the *path* of the body. The conception of a path must include the idea of direction, to express the order in which the body passes through the series of states. With every such change of state there is connected in general a certain amount of work done, W, and of heat received, H, which we may call the *work* and the *heat* of the *path*." "Collected Works," 1, 3 (1928).

[9] "The Theory of Heat," Third Edition, Edited by J. Rogerson Cotter, 19 (1919).

something which can be communicated to matter, and which can be handed on from one piece of matter to another. Heat thus possesses the rank of a *quantity*, and we are led to seek *how much* heat a body gains or loses when its temperature changes. On the other hand, temperature is regarded rather as a quality which varies from one body to another, or from one part to another of the same body, when heat is being communicated to or abstracted from it, or which may vary . . . in consequence of actions taking place within the body itself, or performed on it from without.

"It must, however, be distinctly remembered that what we directly *observe* is temperature and changes of temperature, and when the temperature of a body (free from other actions) rises we *say* it has received heat. The effect observed is the change of temperature, and the postulated cause is addition or subtraction of heat."

The establishment in thermodynamics of the quantitative character of heat is completed by means of calorimetric mixing experiments as explained by Mach;[10] in such experiments it is always found possible to write a "compensation equation" indicating that the heat received (or given up) by the one body in its change of state is equal to the heat given up (or received) by the second body in its simultaneous change of state. This experimental fact is the basis for the introduction of heat as a physical quantity in thermodynamics.

Heat[11] is then analogous to work since work done by one body is always equal to that done on a second body. The double-ended character of a force of course necessitates the conclusion that work is a physical quantity; when the point of application (that is, the point at which the two bodies touch) of the force moves, the work done by the body exerting the force in one direction is equal in magnitude but opposite in sign to that done by the other body.

Now a line integral[12] can be evaluated as an ordinary integral; thus

$$(4) \quad W = \int_{(t_0,p_0)}^{(t,p)} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp = \int_{\sigma_0}^{\sigma} \left[p\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{d\sigma} + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{d\sigma} \right] d\sigma,$$

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[10] E. Mach: "Die Principien der Wärmelehre," 4. Aufl., 182-194 (1923).

The writer is indebted to Professor E. C. Kemble for a clear and cogent development of this topic in his lectures in Physics 6a (a course given in Harvard College), and also for calling the writer's attention to the exposition of Mach.

In numerous books on thermodynamics (for example, Goodenough: "Principles of Thermodynamics," Third Edition, 20 (1920)) it is *proved* that the line integral representing the heat received by a system depends on the path. This proof is based, either explicitly or tacitly, on the postulates of kinetic theory. The argument is that the internal energy depends only on the state of the body and that the work done depends on the path; therefore the heat received, which is equal to the increase in internal energy less the work done, must depend on the path. At the present time it is unnecessary to base the principles of thermodynamics on the postulates of kinetic theory and, for most purposes, it is probably undesirable. The experimental facts of calorimetry discussed by Mach suffice to establish the analytical characterization of heat as a line integral that depends on the path without reference to the postulates of kinetic theory, and this statement is one of the indispensable foundation blocks of the science of empirical thermodynamics.

[11] The developments in this paper are in accord with P. W. Bridgman's illuminating discussion, in terms of experimental operations, of the significance of the quantities, temperature, heat, and energy, in thermodynamics. "The Logic of Modern Physics," 117-131 (1927).

[12] For the definition of the line integral see W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 134-137 (1928).

where σ denotes the parameter that determines the particular series of states through which the system passes, and the path or curve is represented in parametric form by the equations:

(5) (6) $$t = \varphi(\sigma), \quad p = \psi(\sigma).\text{[13]}$$

The line integrals in the definitions of work and heat are functions of the upper limit of integration, σ, and may be differentiated with respect to σ.[14] Thus

(7) $$\frac{dW}{d\sigma} = p\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{d\sigma} + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{d\sigma},$$

and

(8) $$\frac{dQ}{d\sigma} = c_p \frac{dt}{d\sigma} + l_p \frac{dp}{d\sigma}.$$

Multiplying each of these equations by $d\sigma$, one obtains the results,

(9) $$dW = p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp,$$

and

(10) $$dQ = c_p dt + l_p dp,$$

where σ is the independent variable of the functions W and Q and thus $d\sigma = \Delta\sigma$ is the independent (principal) infinitesimal (W and Q are not functions of the independent variables t and p and thus dt and dp are not independent infinitesimals in these equations). The conclusion follows that dQ is just as truly a differential as dv: dv is the differential of a function of two independent variables while dQ is the differential of a function of a single independent variable.

The following statement of Planck concerning dQ has led to much confusion in the literature of thermodynamics, since it is seriously in error and since it has been restated in several text-books. Planck[15] writes:

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[13] If the path be represented by the equation
$$p = f(t),$$
instead of in the parametric form given in the text, then W and Q can be evaluated by the equations,
$$W = \int_{t_0}^{t} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{dt} dt,$$
and
$$Q = \int_{t_0}^{t} c_p(t, f(t)) \, dt + l_p(t, f(t)) \frac{dp}{dt} dt.$$

These two integrals obviously cannot be used to express the work and heat of a straight-line path parallel to the p-axis (change of pressure at constant temperature) and thus these two integrals have a serious disadvantage in comparison with the integrals given in the text. The integrals in the text apply to straight-line paths in all directions as well as to curved paths.

[14] W. F. Osgood: "Advanced Calculus," 215, 216 (1925); E. Goursat: "A Course in Mathematical Analysis," translated by E. R. Hedrick, 1, 154 (1904).

[15] "Vorlesungen über Thermodynamik," 7. Aufl., 55, 56 (1922).

"Nach Clausius' Vorgang wird dieser Ausdruck gewöhnlich, um seine unendliche Kleinheit anzudeuten, mit dQ bezeichnet. Dies hat jedoch nicht selten zu dem Missverständnis Anlass gegeben, als ob die zugeleitete Wärme das Differential einer bestimmten endlichen Grösse Q wäre. Der hierdurch nahe gelegte Trugschluss sei durch folgende kleine Rechnung illustriert. Wählt man T und V als unabhängige Variable, so ist

$$dQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV.$$

Andrerseits ist:

$$dQ = \left(\frac{\partial Q}{\partial T}\right)_V dT + \left(\frac{\partial Q}{\partial V}\right)_T dV.$$

Folglich, da dT und dV voneinander unabhängig sind:

$$\frac{\partial Q}{\partial T} = \frac{\partial U}{\partial T} \quad \text{und} \quad \frac{\partial Q}{\partial V} = \frac{\partial U}{\partial V} + p$$

und daraus durch Differentiation der ersten Gleichung nach V, der zweiten nach T:

$$\frac{\partial^2 Q}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V} + \frac{\partial p}{\partial T},$$

also $\partial p/\partial T = 0$, was sicher unrichtig ist."

It has been proved in this paper that dQ is the differential of a function, Q, of the parameter, σ, that determines the series of states through which the system passes, and that the rigorous definition of a differential is satisfied by dQ.[16] The first part of Planck's statement is therefore erroneous. Moreover in the equation

$$dQ = c_p dt + l_p dp$$

dt and dp are not independent infinitesimals; likewise in the equation

$$dQ = c_v dt + l_v dv$$

dt and dv are not independent infinitesimals, and therefore it does not follow from the latter equation that

$$\frac{\partial^2 U}{\partial t \partial v} = \frac{\partial^2 U}{\partial t \partial v} + \frac{\partial p}{\partial t}.$$

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[16] The same definition of the differential is given in the following works:

W. F. Osgood: "Introduction to the Calculus," 91-93 (1922); "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 236 (1928);

E. Goursat: "A Course in Mathematical Analysis," translated by E. R. Hedrick, 1, 19, 20 (1904);

James Pierpont: "The Theory of Functions of Real Variables," 1, 244 (1905);

E. B. Wilson: "Advanced Calculus," 64 (1912);

F. S. Woods: "Advanced Calculus," 28 (1926);

Cf. also the statement by E. L. Mickelson in his review of D. Humphrey's "Advanced Mathematics for Students of Engineering and Physics" that: "alterations in two or three objectionable statements, of which the most important is the statement that the differential of f(x) is the *actual* change when x is increased by dx, would contribute accuracy well within the student's powers of appreciation." American Mathematical Monthly, **38**, 454 (1931).

In the special cases of straight-line paths parallel to the coordinate axes the reductions of equations (7) and (8) are as follows.

I. Let the path be a straight line in the t,p-plane parallel to the t-axis:

(11) (12) $\qquad t = \sigma, \quad p = K, \quad K$, a constant greater than zero.

Then

(13) $$\frac{dW}{d\sigma} = \frac{dW}{dt} = p\left(\frac{\partial v}{\partial t}\right)_p,$$

and

(14) $$\frac{dQ}{d\sigma} = \frac{dQ}{dt} = c_p.$$

On account of the relation expressed by equation (14), c_p is called the heat capacity at constant pressure.

II. Let the path be a straight line in the t,p-plane parallel to the p-axis:

(15) (16) $\qquad p = \sigma, \quad t = K', \quad K'$, a constant.

Then

(17) $$\frac{dW}{d\sigma} = \frac{dW}{dp} = p\left(\frac{\partial v}{\partial p}\right)_t,$$

and

(18) $$\frac{dQ}{d\sigma} = \frac{dQ}{dp} = l_p.$$

On account of the relation expressed by equation (18), l_p is called the latent heat of change of pressure at constant temperature.

The derivatives

$$\frac{dW}{dt}, \frac{dW}{dp}, \frac{dQ}{dt}, \text{ and } \frac{dQ}{dp}$$

are thus total derivatives, as Professor Kemble[17] has rightly pointed out. Therefore one should not write for them

$$\left(\frac{\partial W}{\partial t}\right)_p, \text{ etc.,}$$

since this notation in mathematics has only one meaning, namely, the partial derivative of a function, W, of the independent variables, t and p, taken with respect to t holding p fast; W and Q are not functions of the independent variables t and p.

Clausius's analytical expression of the first law by means of his equation (58) can be rendered more explicit for reversible processes in the system under consideration by the following equation:

(19) $$U(t,p) - U(t_0,p_0) = \int_{(t_0,p_0)}^{(t,p)} \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right) dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right) dp,$$

which is also written in the more familiar but less explicit form:

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[17] Lectures in Physics 6a.

$$(20) \qquad U(t,p) - U(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} JdQ - dW,$$

the integrals in each of the equations (19) and (20) being extended over any path connecting the points, (t_o,p_o) and (t,p); Q denotes the heat received (heat of the path); W, the work done (work of the path); $J = 1/A$, a constant, the mechanical equivalent of heat; and U, the internal energy per gram measured in mechanical units. The physical hypothesis (experimental fact) embodied in each of the equations, (19) and (20), may be stated in words as follows: The value of the integral in each of the equations, (19) and (20), is independent of the choice of the path of integration, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the internal energy per gram, of the independent variables, t and p. Equation (20) may be brought readily into the form (19) by means of (2) and (3).

From (19) it follows directly that

$$(21) \qquad \left(\frac{\partial U}{\partial t}\right)_p = Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p,$$

and

$$(22) \qquad \left(\frac{\partial U}{\partial p}\right)_t = Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t.$$

Two clear and rigorous proofs of this theorem are given by Osgood.[18]

Substituting the values of $(\partial U/\partial t)_p$ and $(\partial U/\partial p)_t$ just obtained in the equation of the total differential of $U(t,p)$,

$$(23) \qquad dU = \left(\frac{\partial U}{\partial t}\right)_p dt + \left(\frac{\partial U}{\partial p}\right)_t dp,$$

one obtains

$$(24) \qquad dU = \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right) dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right) dp,$$

where t and p are the independent variables of the function U and thus $dt = \triangle t$ and $dp = \triangle p$ are the independent (principal) infinitesimals.

A necessary and sufficient condition for

$$(19) \quad U(t,p) - U(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right) dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right) dp$$

is

$$(25) \qquad \left[\frac{\partial\left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right)}{\partial p}\right]_t = \left[\frac{\partial\left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right)}{\partial t}\right]_p.$$

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[18] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 138-150 (1928).

Two clear and rigorous proofs of this theorem are given by Osgood.[19] Both of these proofs are invaluable in thermodynamics; the first has connections with geometry that render it easily remembered; the second admits immediate extension to systems with more than two independently variable properties and is carried through purely arithmetically (without presupposition of geometric axioms) although it is also interpreted geometrically for ease of comprehension and memory. Equation (25) becomes identical with Clausius's equation (5) if his variable properties y and x that determine the state of the system be identified with t and p. As Clausius[20] pointed out, his equation (5) forms an analytical expression of the first law for reversible changes in a system the state of which is determined by two independent variables, y and x. Thus equation (25) constitutes an analytical expression of the first law for reversible processes in the system considered in this paper.[21]

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[19] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 138-150 (1928).

[20] Op. cit., p. 9.

[21] Lord Kelvin wrote the analogous equation with t and v as the independent variables as the analytical expression of the "first fundamental proposition" or first law of thermodynamics. His statement follows: "Observing that J is an absolute constant, we may put the result into the form

$$\frac{dp}{dt} = J\left(\frac{dM}{dt} - \frac{dN}{dv}\right).$$

This equation expresses, in a perfectly comprehensive manner, the application of the first fundamental proposition to the thermal and mechanical circumstances of any substance whatever, under uniform pressure in all directions, when subjected to any possible variations of temperature, volume, and pressure." Trans. Roy. Soc. Edinburgh, 20, 270 (1851). In the notation of this essay Lord Kelvin's equation would be written:

$$\left(\frac{\partial p}{\partial t}\right)_v = J\left[\left(\frac{\partial l_v}{\partial t}\right)_v - \left(\frac{\partial c_v}{\partial v}\right)_t\right],$$

where l_v denotes the latent heat of change of volume at constant temperature and c_v, the heat capacity at constant volume.

Lippmann has made a similar statement as follows:

"Expression générale du principe de l'équivalence.—En général, dU sera fonction de deux variables indépendantes x et y, de sorte que l'on pourra poser

$$dU = Pdx + Qdy$$

et le principe de l'équivalence sera exprimé par la condition

$$\frac{dP}{dy} = \frac{dQ}{dx}."$$

In the preceding paragraph Lippmann denotes a function of x and y (not the heat received or given up) by Q. He continues farther on:

"Applications du principe de l'équivalence.—I. Soit un kilogramme d'un corps quelconque dont on fait varier le volume et la température en lui faisant parcourir un cycle fermé. Formons l'expression EdQ − dT. On a

$$dQ = cdt + ldv$$

c étant la chaleur spécifique à volume constant, l la chaleur latente de dilatation du corps (quantité de chaleur absorbée par le corps pour que son volume varie d'une quantité égale à l'unité, à température constante);

de plus $dT = pdv,$

donc $dU = E(cdt + ldv) - pdv$

$$dU = E\,cdt + (El - p)dv.$$

"La condition d'intégrabilité est

$$\frac{d(Ec)}{dv} = \frac{d(El - p)}{dt}$$

ou $E\dfrac{dc}{dv} = E\dfrac{dl}{dt} - \dfrac{dp}{dt}$, ou $\dfrac{dp}{dt} = E\left(\dfrac{dl}{dt} - \dfrac{dc}{dv}\right).$

"Cette équation est la traduction du principe de l'équivalence."

Cours de Thermodynamique, Professé à la Sorbonne, par M. Lippmann, Rédigé par MM. E. Mathias et A. Renault, pp. 44, 45 (1889). In the paragraph following the heading "Applications du principe de l'équivalence" Lippmann denotes the heat received by Q and the work done by T.

Equation (20), like (2) and (3), may be differentiated with respect to the parameter σ: thus

$$(26) \qquad \frac{dU}{d\sigma} = J\frac{dQ}{d\sigma} - \frac{dW}{d\sigma}.$$

Multiplying through by $d\sigma$ one obtains

$$(27) \qquad dU = JdQ - dW,$$

where σ is the independent variable of the functions Q, W, and U and thus $d\sigma = \triangle\sigma$ is the independent (principal) infinitesimal. In this equation U
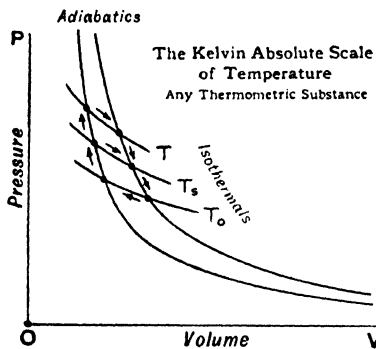
is a function of t and p, but t and p are themselves functions of σ so that U is also a function of σ; in this equation dt and dp are not independent infinitesimals. This equation is given by Clausius as one mathematical statement of the first law. According to Rivett[22] it is the best mathematical statement of the first law, and it is the only analytical expression given by Page.[23] Equation (27) is, however, only a necessary condition and is not a sufficient condition to establish the truth of the first law, since it would still be true even if U were not a function of t and p but

merely equal to the difference, JQ minus W, and, like Q and W, dependent on the choice of the path. Therefore the other forms of Clausius (or the more explicit equivalents of his equations (58) and (5), the present author's (19) and (25)) should be used and not the differential equation (27); the differential equation (27) cannot properly be called an expression of the first law.[24]

The second law of thermodynamics was explained by Clausius[25] as follows:

"Um den zweiten Hauptsatz auf die einfachste Art analytisch auszu-drücken, wollen wir annehmen, die Veränderungen, welche der Körper erleidet, bilden einen *Kreisprocess*, durch welchen der Körper schliesslich wieder in seinen Anfangszustand zurückkommt. Unter dQ sei wieder ein Element der aufgenommenen Wärme verstanden, und T bedeute die vom

[22] A. C. D. Rivett: "The Phase Rule and the Study of Heterogeneous Equilibria," 173 (1923).

[23] Leigh Page: "Introduction to Theoretical Physics," 250 (1928).

[24] In a derivation of the equation of the curve in which a chain hangs between two supports, the catenary curve, Osgood writes: "We use the notation D_x [Osgood here uses Cauchy's notation, $D_{x}y$, for the derivative of y with respect to x] for the derivative advisedly; for, the formulation of the physical problem . . . . leads to *derivatives*, NOT to *differentials*. The latter are introduced later for purely *analytical* reasons. Thus the derivative expresses the thought of physics; the differential is the tool of mathematics." "Advanced Calculus," 319 (1925).

[25] Op. cit., Abhandlung IX.

absoluten Nullpunkte an gezählte Temperatur, welche der Körper in dem Momente hat, wo er dieses Wärmeelement aufnimmt, oder, falls der Körper in seinen verschiedenen Theilen verschiedene Temperaturen hat, die Temperatur des Theiles, welcher das Wärmeelement dQ aufnimmt. Wenn man dann das Wärmeelement durch die dazugehörige absolute Temperatur dividirt, und den dadurch entstehenden Differentialausdruck für den ganzen Kreisprocess integrirt, so gilt für das so gebildete Integral die Beziehung:

(II.)
$$\int \frac{dQ}{T} \lessgtr o,$$

worin das Gleichheitszeichen in solchen Fällen anzuwenden ist, wo alle Veränderungen, aus denen der Kreisprocess besteht, *in umkehrbarer Weise* vor sich gehen, während in solchen Fällen, wo die Veränderungen *in nicht umkehrbarer Weise* geschehen, das Zeichen $<$ gilt. . . .

"Man erhält also für alle umkehrbaren Kreisprocesse die Gleichung:

(IIa.)
$$\int \frac{dQ}{T} = o."$$

Clausius continued farther on:

"Die andere hier in Betracht kommende Grösse, welche sich auf den zweiten Hauptsatz bezieht, ist in der Gleichung (IIa.) enthalten. Wenn nämlich, wie die Gleichung (IIa.) aussagt, das Integral $\int dQ/T$ jedesmal gleich Null wird, so oft der Körper, dessen Veränderungen von irgend einem Anfangszustande beginnen, nach Durchlaufung beliebiger anderer Zustände wieder in den Anfangszustand zurückgelangt, so muss der unter dem Integralzeichen stehende Ausdruck dQ/T das vollständige Differential einer Grösse sein, welche nur vom augenblicklich stattfindenden Zustande des Körpers und nicht von dem Wege, auf welchem er in denselben gelangt ist, abhängt. Bezeichnen wir diese Grösse mit S, so können wir setzen:

(59)
$$dS = \frac{dQ}{T},$$

oder, wenn wir uns diese Gleichung für irgend einem umkehrbaren Vorgang, durch welchen der Körper aus dem gewählten Anfangszustande in seinen gegenwärtigen Zustand gelangen kann, integrirt denken, und dabei den Werth, welchen die Grösse S im Anfangszustande hat, mit S_o bezeichnen:

(60)
$$S = S_o + \int \frac{dQ}{T}.$$

Diese Gleichung ist in ganz analoger Weise zur Bestimmung von S anzuwenden, wie die Gleichung (58) zur Bestimmung von U. . . ."

Clausius obtained an important conclusion, analogous to that obtained in respect to the first law, by the following reasoning:

"In ähnlicher Weise wollen wir nun auch die Gleichung (IIa.) behandeln. Setzen wir in derselben für dQ seinen Werth aus (4) ein, so lautet sie:

$$\int \left(\frac{M}{T} dx + \frac{N}{T} dy \right) = o.$$

Wenn das hier an der linken Seite stehende Integral jedesmal, so oft x und y wieder zu ihren ursprünglichen Werthen gelangen, Null werden soll, so muss der unter dem Integralzeichen stehende Ausdruck das vollständige Differential einer Function von x und y sein, und es muss daher die oben besprochene Bedingungsgleichung der Integrabilität erfüllt sein, welche für diesen Fall folgendermaassen lautet:

$$\frac{d}{dy}\left(\frac{M}{T}\right) = \frac{d}{dx}\left(\frac{N}{T}\right).$$

Führt man hierin die Differentiationen aus, indem man bedenkt, dass die Temperatur T des Körpers ebenfalls als Function von x und y zu betrachten ist, so kommt:

$$\frac{1}{T}\cdot\frac{dM}{dy} - \frac{M}{T^2}\cdot\frac{dT}{dy} = \frac{1}{T}\cdot\frac{dN}{dx} - \frac{N}{T^2}\cdot\frac{dT}{dx},$$

oder anders geordnet:

$$(6) \qquad \frac{dM}{dy} - \frac{dN}{dx} = \frac{1}{T}\left(M\frac{dT}{dy} - N\frac{dT}{dx}\right)."$$

A more explicit form of the analytical expression of the second law given by Clausius in his equation (60) is the following equation for reversible processes in one-component systems consisting of one gaseous phase of unit mass:

$$(28) \qquad S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{c_p}{T}\,dt + \frac{l_p}{T}\,dp,$$

which is also written in the more familiar but less explicit form:

$$(29) \qquad S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{dQ}{T},$$

the integrals in each of the equations (28) and (29) being extended over any path connecting the points (t_o,p_o) and (t,p); T denotes some function of t alone the same for all systems, $T = \omega(t)$; and S denotes the entropy per gram measured in thermal units. The physical hypothesis (experimental fact) embodied in each of the equations, (28) and (29), may be stated in words as follows: The value of each of the integrals in equations (28) and (29) is independent of the choice of the path of integration, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the entropy per gram, of the independent variables, t and p. Equation (29) may be brought readily into the form (28) by means of (3).

From (28) it follows directly[26] that

(30)
$$\left(\frac{\partial S}{\partial t}\right)_p = \frac{c_p}{T},$$

and

(31)
$$\left(\frac{\partial S}{\partial p}\right)_t = \frac{l_p}{T}.$$

Substituting the values of $(\partial S/\partial t)_p$ and $(\partial S/\partial p)_t$ in the equation of the total differential of $S(t,p)$,

(32)
$$dS = \left(\frac{\partial S}{\partial t}\right)_p dt + \left(\frac{\partial S}{\partial p}\right)_t dp,$$

one obtains

(33)
$$dS = \frac{c_p}{T} dt + \frac{l_p}{T} dp,$$

where t and p are the independent variables of the function S and thus $dt = \Delta t$ and $dp = \Delta p$ are the independent (principal) infinitesimals.

A necessary and sufficient condition[27] for

(28)
$$S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{c_p}{T} dt + \frac{l_p}{T} dp,$$

is

(34)
$$\left[\frac{\partial\left(\frac{c_p}{T}\right)}{\partial p}\right]_t = \left[\frac{\partial\left(\frac{l_p}{T}\right)}{\partial t}\right]_p.^{28}$$

If the indicated differentiation be carried out and the result be multiplied by T,

(35)
$$\frac{\partial l_p}{\partial t} - \frac{\partial c_p}{\partial p} = \frac{l_p}{T}\frac{dT}{dt},$$

and if Clausius's y and x be identified with t and p, his equation (6) is obtained. As Clausius[29] pointed out, his equation (6) forms an analytical expression of the second law for reversible processes in a system the state of which is determined by two independent variables, y and x. Thus equation

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[26] Cf. footnote (18).

[27] Cf. footnote (19).

[28] The importance of equations (25) and (34) lies in the fact that from them all of the thermodynamic relations for this system summarized in P. W. Bridgman's "Condensed Collection of Thermodynamic Formulas" (1925) are obtained by direct mathematical methods.

[29] Op. cit., p. 9.

(34) constitutes an analytical expression of the second law for reversible processes in the system considered in this paper.[30]

Equation (29), like (2), (3), and (20), may be differentiated with respect to the parameter σ.
Thus

(36)
$$\frac{dS}{d\sigma} = \frac{1}{T}\frac{dQ}{d\sigma}.$$

Multiplying through by $d\sigma$ one obtains

(37)
$$dS = \frac{dQ}{T},$$

where σ is the independent variable of the functions Q, T, and S and thus $d\sigma = \triangle\sigma$ is the independent (principal) infinitesimal. In this equation T is a function of t, but t is itself a function of σ so that T is also a function of σ; similarly S is a function of t and p, but t and p are themselves functions of σ so that S is also a function of σ; in this equation dt and dp are not independent infinitesimals. This equation is a necessary condition but is not a sufficient condition to establish the truth of the second law; and therefore it cannot properly be called an expression of the second law.

The function $T = \omega(t)$ was used by Lord Kelvin to define a new temperature scale, the absolute thermodynamic scale, which does not depend on the properties of any particular substance. Lord Kelvin's later characterization[31] of the absolute thermodynamic temperature scale is as follows:

"In a communication to the Cambridge Philosophical Society of June, 1848, it was pointed out that any system of thermometry, founded either on equal additions of heat, or equal expansions, or equal augmentations of

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[30] Lippmann has written similarly:

"Pour chercher l'expression analytique de θ, ne fixons pas x et y. Supposons simplement que l'une des deux variables, x, soit une fonction de la température seulement, et varie dans le même sens que la température. Par exemple, x sera donné par un thermomètre à liquide quelconque, inconnu, d'une forme bizarre, irrégulier, astreint à la seule condition que son indication x croisse avec la température. On a alors:

$$dQ = Pdx + Rdy.$$

"P et R seront d'ailleurs des fonctions qui pourront être connues expérimentalement à chaque instant. Alors:

$$dS = \frac{dQ}{\theta} = \frac{P}{\theta}dx + \frac{R}{\theta}dy.$$

"La condition d'intégrabilité qui exprime le principe de Carnot est que:

$$\frac{d\left(\frac{P}{\theta}\right)}{dy} = \frac{d\left(\frac{R}{\theta}\right)}{dx},$$

d'où, en remarquant que θ n'est fonction que de la seule variable x, et que y est indépendant de x,

$$\frac{1}{\theta}\frac{dP}{dy} = \frac{1}{\theta}\frac{dR}{dx} - \frac{R}{\theta^2}\frac{d\theta}{dx},"$$

(Op. cit., pp. 79, 80.) Lippmann here denotes the absolute temperature by θ.

[31] Mathematical and Physical Papers by Sir William Thomson, 1, 393, 394 (1882), or J. P. Joule and W. Thomson: On the Thermal Effects of Fluids in Motion, Part II, Phil. Trans., 144, 350-352 (1854).

pressure, must depend on the particular thermometric substance chosen, since the specific heats, the expansions, and the elasticities of substances vary, and, so far as we know, not proportionally with absolute rigour for any two substances. . . . It appears then that the standard of practical thermometry consists essentially in the reference to a certain numerically expressible quality of a particular substance. In the communication alluded to, the question, 'Is there any principle on which an absolute thermometric scale can be founded?' was answered by showing that Carnot's function[32] (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of Carnot's function, may be defined as temperature, and is therefore the foundation of an absolute system of thermometry. . . . and we may define temperature simply as the reciprocal of Carnot's function. When we take into account what has been proved regarding the mechanical action of heat, and consider what is meant by Carnot's function, we see that the following explicit definition may be substituted:—

"*If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of the operations.*

"To fix on a unit or degree for the numerical measurement of temperature, we may either call some definite temperature, such as that of melting ice, unity, or any number we please; or we may choose two definite temperatures, such as that of melting ice and that of saturated vapour of water under the pressure 29.9218 inches of mercury in the latitude of 45°, and call the difference of these temperatures any number we please, 100 for instance. . . . it becomes a question, what is the temperature of melting ice, if the difference between it and the standard boiling-point be called 100°?"

Lord Kelvin's definition of the absolute thermodynamic temperature scale is related to equation (29) as follows. For a Carnot cycle of operations of a reversible thermodynamic engine (a closed cycle consisting of two isothermal and two adiabatic transformations), with any working fluid, equation (29) takes the form

(38)
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0,$$

where T_1 denotes the absolute temperature of the upper isotherm of the Carnot cycle (temperature of the heat reservoir); T_2, the absolute temperature

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[32] Carnot's function, η, is the amount of work done per unit of heat received by a Carnot engine operating in cycles between a heat source and a heat sink that differ in temperature by one degree absolute. It may be proved easily from equations (20) and (29) of this paper that

$$\frac{\eta}{J} = \frac{Q' + Q''}{Q'} = \frac{W}{JQ'} = \frac{T' - T''}{T'} = \frac{1}{T'},$$

where Q' denotes the heat absorbed (a positive quantity) by the working fluid of the Carnot engine at the temperature T'; Q'', the heat absorbed (a negative quantity) at the temperature T''; W, the work done; T', the absolute temperature of the heat source; and T'', the absolute temperature of the heat sink. In regard to the definition of Carnot's function cf. Mathematical and Physical Papers by Sir William Thompson 1, 224, 225, 391, 397.

of the lower isotherm (temperature of the heat sink); Q_1, the heat absorbed (a positive quantity) at the temperature T_1; and Q_2, the heat absorbed (a negative quantity) at the temperature T_2. Thus for the segments of three isotherms at the arbitrary temperature T, and the fixed temperatures T_o and T_s, one has

$$(39) \qquad \frac{Q}{T} = \frac{Q_s}{T_s} = -\frac{Q_o}{T_o}$$

provided all three segments of isotherms connect the same pair of adiabatics (as illustrated in Fig. 1). The temperature T_o is that of ice melting under the pressure of one atmosphere and T_s that of saturated vapor of water boiling under the pressure of one atmosphere. In the case discussed T is assumed to be greater than T_o. Now let both sides of the equation

$$(40) \qquad \frac{Q_s}{T_s} = -\frac{Q_o}{T_o}$$

be multiplied by $T_s T_o$; the result is

$$(41) \qquad Q_s T_o = -Q_o T_s.$$

To each side of this equation let $Q_o T_o$ be added

$$(42) \qquad Q_s T_o + Q_o T_o = -Q_o T_s + Q_o T_o;$$
thus
$$(43) \qquad T_o (Q_s + Q_o) = -Q_o (T_s - T_o),$$
and hence

$$(44) \qquad -\frac{T_o}{Q_o} = \frac{T_s - T_o}{Q_s + Q_o}.$$

From (39) one has

$$(45) \qquad \frac{T}{Q} = -\frac{T_o}{Q_o}.$$

Therefore

$$(46) \qquad \bullet \qquad \frac{T}{Q} = \frac{T_s - T_o}{Q_s + Q_o}.$$

The difference $T_s - T_o$ is defined as $100°$.
Hence finally

$$(47) \qquad T = \frac{100\ Q}{Q_s + Q_o},$$

where Q, Q_s, and Q_o denote heat absorbed and Q and Q_s are thus positive quantities and Q_o a negative quantity in the case discussed. This equation determines the absolute temperature in terms of heat quantities; and the heat quantities can be measured, in theory, by means of a hydrogen thermometer and calorimeter. In practice this method of evaluating the absolute temperature is replaced by one founded on the Joule-Thomson coefficient (porous plug effect). The equation required in the latter method is derived in the following paragraphs.

The evaluation of the absolute temperature by the determination of the Joule-Thomson coefficient (porous plug effect), together with data for the heat capacity and specific volume of the thermometric substance, is accomplished by means of equations (25) and (35). From (25) one has

$$(48) \qquad J\left(\frac{\partial l_p}{\partial t}\right)_p = J\left(\frac{\partial c_p}{\partial p}\right)_t - \left(\frac{\partial v}{\partial t}\right)_p.$$

From (48) is subtracted (35) multiplied by J

$$J\left(\frac{\partial l_p}{\partial t}\right)_p - J\frac{l_p}{T}\frac{dT}{dt} = J\left(\frac{\partial c_p}{\partial p}\right)_t;$$

thus

$$(49) \qquad \frac{1}{T}\frac{dT}{dt} = -\frac{\left(\frac{\partial v}{\partial t}\right)_p}{Jl_p}.$$

The Joule-Thomson coefficient, μ, is defined by the equation

$$(50) \qquad \mu = \left(\frac{\partial t}{\partial p}\right)_\chi,$$

where χ denotes Gibbs's chi function or the total heat (also called heat content, enthalpy, enkaumy). The function χ is defined by the equation

$$(51) \qquad \chi = U + pv,$$

and is thus a function of the temperature and pressure:

$$(52) \qquad \chi = U(t,p) + p\ v(t,p) = \Gamma(t,p).$$

It is of course assumed in the definition of the Joule-Thomson coefficient, μ, that the equation

$$\chi = U + pv$$

can be solved for t in terms of p and χ : $t = \Psi(p,\chi)$. Then one has

$$(52) \qquad \chi = \Gamma(t,p) \qquad \left\{\begin{array}{l}\text{Independent variables of the} \\ \text{1st class, (t,p);} \qquad \bullet\end{array}\right.$$

$$(53)\ (54)\quad p = p,\ t = \Psi(p,\chi) \qquad \left\{\begin{array}{l}\text{Independent variables of the} \\ \text{2nd class, (p,}\chi\text{).}\end{array}\right.$$

To these equations the theorem for change of variables in partial differentiation is applied and thereby the result obtained:

$$(55) \qquad \left(\frac{\partial \chi}{\partial p}\right)_\chi = \left(\frac{\partial \chi}{\partial t}\right)_p\left(\frac{\partial t}{\partial p}\right)_\chi + \left(\frac{\partial \chi}{\partial p}\right)_t\left(\frac{\partial p}{\partial p}\right)_\chi,\ ^{33}$$

or

$$(56) \qquad 0 = \left(\frac{\partial \chi}{\partial t}\right)_p\left(\frac{\partial t}{\partial p}\right)_\chi + \left(\frac{\partial \chi}{\partial p}\right)_t.$$

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[33] Cf. W. F. Osgood: "Advanced Calculus," Chapter V, Section 14, "A Question of Notation" and Exercise 3, p. 141. Section 14 was written with particular reference to problems of thermodynamics such as the one here at issue and is the clearest statement of the solution of this problem known to the present writer.

From the equation of definition of χ and equations (21), (22), and (56), it follows that

$$(57) \qquad \left(\frac{\partial t}{\partial p}\right)_\chi = -\frac{\left(\frac{\partial \chi}{\partial p}\right)_t}{\left(\frac{\partial \chi}{\partial t}\right)_p} = -\frac{J\,l_p + v}{Jc_p}.$$

Hence

$$(58) \qquad J\,l_p = -\,Jc_p\left(\frac{\partial t}{\partial p}\right)_\chi - v.$$

Substituting this value of l_p in equation (49) one obtains

$$(59) \qquad \frac{d\log_e T}{dt} = \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_\chi}.$$

Integrating this equation one obtains

$$(60) \qquad \log_e \frac{T}{T_0} = \int_{(t_0,p_0)}^{(t,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + J\,c_p\left(\frac{\partial t}{\partial p}\right)_\chi}\,dt.$$

The integrand is a function of the temperature, t, alone, and does not vary with the pressure, p; the integral may therefore be evaluated along the path in the t,p-plane followed by the thermometric substance in the constant volume hydrogen thermometer. Let the value of e raised to the power the integral between $t_0 = 0°C.$ and $t_s = 100°C.$ be denoted by G:

$$(61) \qquad \frac{T_s}{T_0} = G = e^{\displaystyle\int_{(t_0,p_0)}^{(t_s,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_\chi}\,dt}.$$

Since, by definition

$$(62) \qquad T_s - T_0 = 100,$$

therefore

$$(63) \qquad T_0 = \frac{100}{G-1}.$$

Hence finally

$$(64) \qquad T = \omega(t) = \frac{100}{G-1}\,e^{\displaystyle\int_{(t_0,p_0)}^{(t,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_\chi}\,dt}.$$

The integrand and the constant, G, can be determined experimentally. To evaluate the constant, G, that is, the value of e raised to the power the integral in equation (61) between the fixed limits, t_0 and t_s, the integrand

must be determined experimentally between t_o and t_s. To evaluate $T = \omega(t)$ if t lies above t_s, the integrand in equation (64) must be determined experimentally in the interval (t_s,t) in addition to the interval (t_o,t_s). Similarly to evaluate $T = \omega(t)$ if t lies below t_o, the integrand in equation (64) must be determined experimentally in the interval (t,t_o) in addition to the interval (t_o,t_s).[34]

Numerous investigations of one-component systems of one phase are recorded in the literature and it is not necessary to discuss such a system in detail in this paper. Especially notable is the recent work on the one-component system, H_2O, which is important in applications of thermodynamics in many fields, from power generation to geochemistry. N. F. Osborne[35] has stated that: "The most formidable problem in the preparation of a thermodynamic table or chart for a given substance is to obtain data adequate as to kind, range, and accuracy." The data for the system, H_2O, to which Osborne has contributed so much himself, are based on numerous and consistent measurements that have been improved and greatly extended since 1921. Thus J. H. Keenan[36] has written: "the demand for steam data at still higher pressures and temperatures [than 1200 lb. per sq. in. and 800 deg. Fahr.] has been steadily growing. The additional experimental data recently obtained at the Massachusetts Institute of Technology and at the Bureau of Standards have made possible the development of a complete set of steam tables and diagrams to 3500 lb. per sq. in. and 1000 deg. Fahr. A year ago the Turbine Engineering Department of the General Electric Company undertook this development. The necessary data and many valuable suggestions were obtained from those engaged in the Steam Research Program, and the successful completion of the work is in no small degree due to their cooperation.

"Sources of data. The Harvard Joule-Thomson-effect experiments which extended to 565 lb. per sq. in. and 657 deg. Fahr. had been carefully studied and reformulated by Dr. Davis during 1926 and 1927, and the new formulation was used in this development. It differed only slightly from the older formulation that was used in the work of 1925, but it embodied certain concepts which guided extrapolation.

"The Knoblauch specific-heat measurements extending to 420 lb. per sq. in. were used as in the work of 1925 to supplement the Harvard data.

"In 1927 Dr. Keyes and Dr. Smith at the Massachusetts Institute of Technology completed a set of experimental determinations of the specific volume of superheated steam between 1350 lb. per sq. in. and 3850 lb. per sq. in., and between saturation and 752 deg. Fahr. They constitute the basis of the development between 1000 lb. per sq. in. and 3500 lb. per sq. in.

[34] For numerical data and bibliography see Arthur L. Day and R. B. Sosman: Realisation of Absolute Scale of Temperature, "A Dictionary of Applied Physics," Edited by Sir Richard Glazebrook, 1, 836-871 (1922).

[35] Trans. Am. Soc. Mech. Engineers, Fuels and Steam Power, 52, 221 (1930).

[36] Mechanical Engineering, 51, 109, 114 (1929).

"The same experimenters had determined the pressure-temperature relationship at saturation up to the critical point. These data, which agree closely with the Reichsanstalt experiments, were used in this development.

"The Bureau of Standards contributed two very important pieces of data: (1) The mechanical equivalent of heat reported by Dr. Osborne in December, 1927, namely, 1 mean B.t.u. = 778.57 ft-lb. . . . (2) The total heat of saturated water between 32 deg. Fahr. and 482 deg. Fahr. (0.09 lb. per sq. in. and 577 lb. per sq. in.), communicated privately with the permission of the Director of the Bureau. Other experimenters contributed minor parts at various stages of the work, but the development was primarily dependent on those mentioned. . . .

"It is hoped that in the interim [before the goal of an international table is attained] this steam table . . . . will fill the need for a tabulation of the properties of steam covering the critical region and offering both thermodynamic consistency and faithfulness to reliable experimental data.

"It has served to bring to light the remarkable agreement between the experimental results of the three parts of the A. S. M. E. program, and between these results and other high-grade experimental data. It has shown the agreement between work done both by continuous-flow and static methods."

Keenan[37] has subsequently made a comparison of his table and Mollier chart with more recent experimental data. Concerning this comparison he writes as follows:

"The steam table and chart presented . . . . were based on all the experimental data available in April, 1928. Since that time the experimental progress includes a complete experimental check of the Keyes-Smith data which verifies the original values within a few hundredths of 1 per cent; an extension of the Bureau of Standards liquid total heats from 600 lb. per sq. in. to 800 lb. per sq. in.; the Masaryk total-heat measurements; and, most notably, an extension of the Knoblauch specific heats from 420 lb. per sq. in. to 1750 lb. per sq. in. In days like these, steam tables must be well founded to stand the test of the next six months' work. . . .

"The Knoblauch measurements almost completely cover a large range of pressures where the properties of steam could be determined six months ago only by extrapolation of existing experimental data. The new tables represent such an extrapolation, and it is very interesting to compare specific heats computed from them with these new measurements from Germany. The agreement is so good as to justify confidence in these tables even through the range not covered by experiment at the time they were computed. It indicates a fundamental agreement between experimental results obtained at Munich by one method with those obtained at M. I. T. and Harvard by entirely different methods. . . . The evidence at hand shows a general con-

[37] Mechanical Engineering, 51, 129 (1929).

vergence on a well-defined grid of data that will ultimately constitute the international standard."[38]

In concluding this paper one may pause briefly at the part of the boundary of thermodynamics where Clausius labored to construct lines of communication into the adjoining region of atomistics, to consider the fact that Clausius and most investigators since his time have not been content with the evaluation of the relations of thermodynamics and the measurement of thermodynamic quantities, but in addition have correlated thermodynamics with atomistics in various ways. For this purpose the well-known explanations of temperature and heat in terms of atomic properties have been developed. Thus H. A. Bumstead[39] has written:

"[In his earliest publications Gibbs] had been concerned with the development of the consequences of the laws of thermodynamics which are accepted as given by experience; in this empirical form of the science, heat and mechanical energy are regarded as two distinct entities, mutually convertible of course with certain limitations, but essentially different in many important ways. In accordance with the strong tendency toward unification of causes, there have been many attempts to bring these two things under the same category; to show, in fact, that heat is nothing more than the purely mechanical energy of the minute particles of which all sensible matter is supposed to be made up, and that the extra-dynamical laws of heat are consequences of the immense number of independent mechanical systems in any body,—a number so great that, to human observation, only certain averages and most probable effects are perceptible."

The last work of Gibbs is his elaboration of these problems, entitled "Elementary Principles in Statistical Mechanics developed with especial reference to the Rational Foundation of Thermodynamics." However, according to Bumstead, "Gibbs has not sought to give a mechanical explanation of heat, but has limited his task to demonstrating that such an explanation is possible."[40]

These correlations are undoubtedly of very great importance and value, as are, in general, attempts to connect the various fields of science. The fundamental principles of thermodynamics may still be taken as empirical results of experience, however, since sufficient experimental data are available to establish them without reference to the laws of atomistics. And it is probably fortunate in some ways that this is so, because many problems in thermodynamics and its applications in power generation, geochemistry, and other fields, are therefore capable of solution where adequate atomistic data

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[38] Among the further developments with this system are the "Skeleton Steam Tables" prepared at the International Steam-Table Conference of physicists and engineers from America, Great Britain, Germany, and Czechoslovakia, held in London during July, 1929. In these Tables are given mean values of the properties of saturated and superheated steam, with a plus or minus tolerance attached to each value, which, with the tolerances of the agreed magnitudes, were unanimously accepted by the delegates. Mechanical Engineering, **52**, 120-122 (1930).

[39] "The Collected Works of J. Willard Gibbs," 1, 23, 25 (1928), or Am. J. Sci., (4) **16**, 197, 199 (1903).

[40] Footnote on page 1768.

are lacking. Thus temperature as that which is measured by means of the gas thermometer and thermocouple, heat as that which is measured in the calorimeter, and thermodynamics as the science of heat and work, still serve as powerful artillery in several advancing sectors of science and technology.

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Appendix

Statement by Lord Kelvin of the history of the first and second laws of thermodynamics.

(Extracts from Lord Kelvin's paper entitled "On the Dynamical Theory of Heat.")[41]

"3. The recent discoveries made by Mayer and Joule, of the generation of heat through the friction of fluids in motion, and by the magneto-electric excitation of galvanic currents, would either of them be sufficient to demonstrate the immateriality of heat; and would so afford, if required, a perfect confirmation of Sir Humphry Davy's views.

"4. Considering it as thus established, that heat is not a substance, but a dynamical form of mechanical effect, we perceive that there must be an equivalence between mechanical work and heat, as between cause and effect. The first published statement of this principle appears to be in Mayer's *Bemerkungen über die Kräfte der unbelebten Natur*, which contains some

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[40] In this connection it seems worth while to quote the following from Gibbs's "Elementary Principles in Statistical Mechanics" ("The Collected Works of J. Willard Gibbs," **2**, part 1, 165, 166, 167):

"If we wish to find in rational mechanics an *a priori* foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy. . . .

"At least, we have to show by *a priori* reasoning that for such systems as the material bodies which nature presents to us, these relations hold with such approximation that they are sensibly true for human faculties of observation. This indeed is all that is really necessary to establish the science of thermodynamics on an *a priori* basis. Yet we will naturally desire to find the exact expression of those principles of which the laws of thermodynamics are the approximate expression. A very little study of the statistical properties of conservative systems of a finite number of degrees of freedom is sufficient to make it appear, more or less distinctly, that the general laws of thermodynamics are the limit toward which the exact laws of such systems approximate, when their number of degrees of freedom is indefinitely increased. . . .

"The enunciation and proof of these exact laws, for systems of any finite number of degrees of freedom, has been a principal object of the preceding discussion. But it should be distinctly stated that, if the results obtained when the numbers of degrees of freedom are enormous coincide sensibly with the general laws of thermodynamics, however interesting and significant this coincidence may be, we are still far from having explained the phenomena of nature with respect to these laws. For, as compared with the case of nature, the systems which we have considered are of an ideal simplicity. . . .

"The ideal case of systems of a finite number of degrees of freedom remains as a subject which is certainly not devoid of a theoretical interest, and which may serve to point the way to the solution of the far more difficult problems presented to us by nature."

[41] Trans. Roy. Soc. Edinburgh, **20**, 261-267 (1851), or "Mathematical and Physical Papers," 1, 174-181 (1882).

correct views regarding the mutual convertibility of heat and mechanical effect, along with a false analogy between the approach of a weight to the earth and a diminution of the volume of a continuous substance, on which an attempt is founded to find numerically the mechanical equivalent of a given quantity of heat. In a paper published about fourteen months later, 'On the Calorific Effects of Magneto-Electricity and the Mechanical Value of Heat,' Mr. Joule, of Manchester, expresses very distinctly the consequences regarding the mutual convertibility of heat and mechanical effect which follow from the fact, that heat is not a substance but a state of motion; and investigates on unquestionable principles the 'absolute numerical relations,' according to which heat is connected with mechanical power; verifying experimentally, that whenever heat is generated from purely mechanical action, and no other effect produced, whether it be by means of the friction of fluids or by the magneto-electric excitation of galvanic currents, the same quantity is generated by the same amount of work spent; and determining the actual amount of work, in foot-pounds, required to generate a unit of heat, which he calls 'the mechanical equivalent of heat.' . . .

"9. The whole theory of the motive power of heat is founded on the two following propositions, due respectively to Joule, and to Carnot and Clausius.

"Prop. I. (Joule).—When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.

"Prop. II. (Carnot and Clausius).—If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermo-dynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat. . . .

"12. The demonstration of the second proposition is founded on the following axiom:—

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

"13. To demonstrate the second proposition, let A and B be two thermo-dynamic engines, of which B satisfies the conditions expressed in the enunciation; and let, if possible, A derive more work from a given quantity of heat than B, when their sources and refrigerators are at the same temperatures, respectively. Then on account of the condition of complete *reversibility* in all its operations which it fulfils, B may be worked backwards, and made to restore any quantity of heat to its source, by the expenditure of the amount of work which, by its forward action, it would derive from the same quantity of heat. If, therefore, B be worked backwards, and made to restore to the source of A (which we may suppose to be adjustable to the engine B) as much heat as has been drawn from it during a certain period of the working of A,

a smaller amount of work will be spent thus than was gained by the working of A. Hence, if such a series of operations of A forwards and of B backwards be continued, either alternately or simultaneously, there will result a continued production of work without any continued abstraction of heat from the source; and, by Prop. I., it follows that there must be more heat abstracted from the refrigerator by the working of B backwards than is deposited in it by A. Now it is obvious that A might be made to spend part of its work in working B backwards, and the whole might be made self-acting. Also, there being no heat either taken from or given to the source on the whole, all the surrounding bodies and space except the refrigerator might, without interfering with any of the conditions which have been assumed, be made of the same temperature as the source, whatever that may be. We should thus have a self-acting machine, capable of drawing heat constantly from a body surrounded by others at a higher temperature, and converting it into mechanical effect. But this is contrary to the axiom, and therefore we conclude that the hypothesis that A derives more mechanical effect from the same quantity of heat drawn from the source than B is false. Hence no engine whatever, with source and refrigerator at the same temperatures, can get more work from a given quantity of heat introduced than any engine which satisfies the condition of reversibility, which was to be proved.

"14. This proposition was first enunciated by Carnot, being the expression of his criterion of a perfect thermo-dynamic engine. He proved it by demonstrating that a negation of it would require the admission that there might be a self-acting machine constructed which would produce mechanical effect indefinitely, without any source either in heat or the consumption of materials, or any other physical agency; but this demonstration involves, fundamentally, the assumption that, in 'a complete cycle of operations,' the medium parts with exactly the same quantity of heat as it receives. A very strong expression of doubt regarding the truth of this assumption, as a universal principle, is given by Carnot himself; and that it is false, where mechanical work is, on the whole, either gained or spent in the operations, may (as I have tried to show above) be considered to be perfectly certain. It must then be admitted that Carnot's original demonstration utterly fails, but we cannot infer that the proposition concluded is false. The truth of the conclusion appeared to me, indeed, so probable that I took it in connexion with Joule's principle, on account of which Carnot's demonstration of it fails, as the foundation of an investigation of the motive power of heat in air-engines or steam-engines through finite ranges of temperature, and obtained about a year ago results, of which the substance is given in the second part of the paper at present communicated to the Royal Society. It was not until the commencement of the present year that I found the demonstration given above, by which the truth of the proposition is established upon an axiom (§ 12) which I think will be generally admitted. It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius, who published

his demonstration of it in the month of May last year, in the second part of his paper on the motive power of heat. I may be allowed to add, that I have given the demonstration exactly as it occurred to me before I knew that Clausius had either enunciated or demonstrated the proposition. The following is the axiom on which Clausius' demonstration is founded:—

"It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.

"It is easily shown, that, although this and the axiom I have used are different in form, either is a consequence of the other. The reasoning in each demonstration is strictly analogous to that which Carnot originally gave."

Geophysical Laboratory,
Carnegie Institution of Washington,
March, 1932.

THE PYROLYSIS OF METALLIC ARSENITES

BY EUGENE RAY RUSHTON

Introduction

Simon[1] found that, when heated, calcium pyro-arsenite, $(CaO)_2.As_2O_3$, and calcium meta-arsenite, $CaO.As_2O_3$, gave elemental arsenic and calcium arsenate, part of the arsenite having been oxidized and part reduced. Magnesium arsenite was found to react similarly; but the reaction apparently did not take place to the same extent as with calcium arsenite. When lead oxide was treated with the vapor of arsenious oxide, the mass melted and the lead arsenite, thus formed, was not changed by further heating under the conditions of his experiment. Ferric arsenite was found to give off the vapor of arsenious oxide, leaving a magnetic residue probably magnetite. This could not, of course, be the whole story as such a reaction would not balance. Copper arsenite, when heated, gave arsenious oxide, copper arsenate, and a residue insoluble in nitric acid containing copper and arsenic. Silver arsenite gave arsenious oxide, silver arsenate, and metallic silver free from arsenic.

According to Brame,[2] heating powdered baryta with arsenious oxide causes the formation of barium arsenate and metallic arsenic. Similar results were obtained with potassium and sodium hydroxides; but were less marked.

Tammann[3] determined the heating curves of equimolecular mixtures of arsenious oxide with various metallic oxides. With calcium oxide about fifty percent of the oxides combined to form arsenite when heated to 300°. At 465° some arsenious oxide vaporized and at 468° a rapid exothermal reaction took place with the separation of elemental arsenic. The results for 300° are not equilibrium data. Calcium oxide, arsenious oxide, and a compound of the two can only coexist as three solid phases in equilibrium at a single temperature, the inversion point and there is no reason to suppose that there is any such temperature, though this is not theoretically impossible.

No metallic arsenic was formed when magnesium oxide was heated in a similar manner with an equimolecular quantity of arsenious oxide. The meta-arsenite, when heated further, lost some of its arsenious oxide. Zinc oxide combined with the arsenious oxide to form the meta-arsenite, from which arsenious oxide vaporized when heated higher. With nickel oxide apparently the ortho-arsenite was formed, leaving two-thirds of the arsenious oxide uncombined. With copper oxide the arsenious oxide reacted at 410° to form cuprous arsenate.

[1] Pogg. Ann., **40**, 417 (1837).
[2] Compt. rend., **92**, 188 (1881).
[3] Z. anorg. allgem. Chem., **149**, 84 (1925).

Tammann's experiments show that only calcium arsenite reacts to form metallic arsenic and that even calcium arsenite shows some tendency to dissociate into its constituent oxides. According to Simon, magnesium arsenite also decomposes to give some metallic arsenic, while Tammann did not get this result. The difference may be due to a difference in the compositions of the arsenites. Tammann's mixture probably contained more arsenious oxide than the substance with which Simon was working and may therefore have permitted a more ready vaporization of arsenious oxide. On the other hand the difference may have been in the rate of heating. Calcium arsenite apparently reacts to form calcium arsenate and metallic arsenic at a temperature only slightly above the temperature of thermal dissociation. With magnesium arsenite there is probably a greater difference between the initial temperature of thermal dissociation and that of oxidation-reduction. Tammann may not have heated his magnesium arsenite to the temperature at which the arsenious oxide is decomposed. This latter explanation cannot be true if equilibrium conditions were maintained; and it presupposes that arsenious oxide decomposes, an assumption for which there is no satisfactory evidence.

The tendency of arsenious oxide in combination to undergo oxidation-reduction seems to be greater the more basic the oxide with which it is combined. This may be due to the initial temperature of the reaction being lower for the arsenites of the more basic elements, or to a more rapid reaction at a given temperature. On the other hand it may be due to the presumably greater thermal stability of the arsenates of the more basic metals, since the decomposition of the arsenate formed would tend to reverse the reaction.

Arsenates are, in general, known to be more stable towards heat than the corresponding arsenites. Simon found calcium arsenate to be unchanged at red heat. Mitscherlich[1] found that sodium and potassium arsenates did not decompose until above $1100°$ when heated in a stream of nitrogen. Calcium arsenate was found to decompose at bright red heat with the liberation of oxygen and arsenious oxide. Other arsenates (not specified) were found to decompose at dull red heat. Herbst[2] found that potassium meta-arsenate $K_2O.As_2O_5$, could be heated for hours over the Bunsen burner without decomposing. This apparent contradiction may be due to the tendency of the oxygen of the air to reverse the decomposition of the arsenate into arsenious oxide and oxygen. From the data available it is not possible to determine whether or not the stability of the resulting arsenate has any effect on the oxidation-reduction reaction.

The presence of bases in solution is known to accelerate the oxidation of dissolved arsenious oxide by air.[3] On the other hand, arsenates are more easily reduced by potassium iodide in acid solution. The first is merely another illustration of the well-known fact that reducing agents are stronger in alkaline than in acid solutions. Other instances of the same type are alkaline pyrogallol and all the photographic developers. The other is due to the

[1] Ann. Chim. Phys., (6) **27**, 22 (1892).
[2] Inaugural Diss. Berne University (1894).
[3] Cf. Berthelot: Bull., **28**, 496 (1877).

fact, which we could not have predicted, that the oxidizing potential of hydriodic acid is increased more by acids than the reducing potential of arsenious oxide is decreased thereby.

There is no indication in the literature that arsenious ox'de shows any tendency to undergo oxidation-reduction when heated alone. Hautefeuille[1] states that arsenious acid, when heated with hydrogen gives arsenic acid—and presumably metallic arsenic, since he states that sulphurous acid gives sulphuric acid and sulphur. Damm and Kraff[2] found that antimonous oxide, when heated to $1050°$ in an evacuated tube, decomposed completely according to the equation

$$4\ Sb_4O_6 = 3\ Sb_4O_3 + 4\ Sb.$$
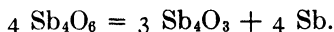
However, Biltz[3] determined the vapor density of arsenious oxide up to $1800°$ and did not report any decomposition, only depolymerization according to the equation

$$As_4O_6 = 2\ As_2O_3.$$
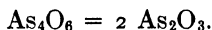
It appears therefore that the oxidation-reduction of arsenious oxide is brought by the basic oxide and is not simply catalyzed by it.

According to Wanklyn[4] arsenious oxide decomposes in the presence of strongly basic substances according to the equation

$$5\ As_2O_3 = 3\ As_2O_5 + As_4;$$
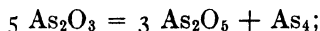
but he gives no experimental evidence to prove this. Sulphites have been found by Foerster and Kubel[5] and by Zawidski[6] to decompose according to the equation.

$$4\ M_2SO_3 = 3\ M_2\ SO_4 = M_2S.$$

This equation is reversible, probably because both of the reaction products are solid.

There is the possibility that arsenides are formed when arsenites decompose. However, arsenic is more electro-positive than sulphur and would therefore have less tendency to combine with the metal. Soubeiran[7] stated that when basic oxides and elemental arsenic are heated together, arsenites and arsenides are formed; but he gave no conclusive evidence of the presence of the metallic arsenides. Moser and Marian[8] found that the arsenates of sodium, barium, and strontium could be freed completely of their arsenic by heating with ammonium chloride; but that the arsenates of calcium and magnesium were much more difficult to decompose in this way. They attempted to explain this as due to the formation of an arsenide.

[1] Bull., (2) **7**, 206 (1867).

[2] Ber., **40**, 4774 (1907).

[3] Z. physik. Chem., **19**, 419 (1896).

[4] "Arsenic," 21 (1901).

[5] Z. anorg. allgem. Chem., **139**, 261 (1924).

[6] Roczniki Chem., **52**, 488 (1925).

[7] Ann. Chim. Phys., (2) **43**, 407 (1830).

[8] Ber., **59B**, 1335 (1926).

Arsenides of the alkaline earth metals and of lithium have been prepared by Lebeau[1] heating the arsenates with carbon in the electric furnace. He found that these substances, when heated in the air, give the arsenates. They liberate arsine when placed in cold water. These arsenides are apparently not volatile at the temperature of the electric furnace and so there would be no volatile products if all the arsenic formed arsenide. There is no conclusive evidence that there is not some arsenide formed.

Amat[2] found that acid phosphites are difficult to dehydrate without oxidizing or decomposing. When sodium acid phosphite was heated at $150°$-$160°$ the following reaction took place:

$$2 \ NaH_2PO_3 = Na_2H_2P_2O_5 + H_2O.$$
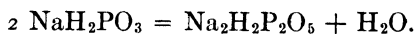
When the acid pyrophosphite, thus formed, was heated to $200°$, it began to decompose and the decomposition was found to be complete at dull red heat according to the equation

$$5 \ Na_2H_2P_2O_5 = 2 \ PH_3 + 2 \ H_2 + Na_4P_2O_7 + 6 \ NaPO_3.$$
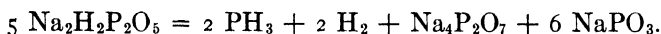
In the case of the barium salt and similar substances, Amat found that the odor of phosphine became noticeable when the residue was placed in water or in acid, from which he concluded that a little metallic phosphide is formed, as the phosphides of the alkalies and alkaline earths are known to be hydrolyzed by water. No data appear to be available on the thermal decomposition of anhydrous phosphites; but they would probably form elemental phosphorus.

Thénard[3] found that, when phosphorus and lime are heated together, a large amount of the phosphorus reacts with the lime, the residue consisting of calcium phosphate and phosphide, apparently $Ca_2P_2O_7$ and Ca_2P. He found that the phosphide reacted with water to give the liquid phosphine $(PH_2)_n$. From the similarity between arsenic and phosphorus, it seems quite probable that Soubeiran obtained some arsenide when he heated elemental arsenic with basic oxides. The presence of any appreciable amount of arsenide of the formula M_3As would be immediately evident if the residue were placed in water, due to the liberation of arsine; but arsenides containing a smaller proportion of metal might well yield a solid hydride of arsenic containing less hydrogen than arsenic and having no appreciable odor. Such hydrides contain only about one percent of hydrogen and consequently not much error would be introduced if they were considered to be pure arsenic.

Bloxam[4] observed the liberation of a small amount of arsine when arsenious oxide in excess was heated with an alkali. When the alkali was in excess, pure hydrogen was liberated and the arsenious oxide was oxidized to arsenate by the oxygen of the water. Since Regnault[5] found that there is practically no formation of hydrogen when elemental arsenic is heated to redness in contact with water vapor, the reaction must be due to the presence of the base.

[1] Bull., (3) **21**, 769 (1899).
[2] Ann. Chim. Phys., (6) **24**, 324 (1891).
[3] Ann. Chim. Phys., (3) **14**, 5 (1845).
[4] J. Chem. Soc., **15**, 281 (1862).
[5] Ann. Chim. Phys., (2) **62**, 364 (1836).

If any of the arsenic hydrides should be formed during the pyrolysis of an arsenite they would be decomposed quickly into arsenic and hydrogen, and the decomposition would be made visible by the arsenic deposited. On the other hand the evolution of hydrogen would not be so obvious and the presence of arsenate would not be apparent without some analytical test. Complete dehydration of the arsenites employed in these experiments is therefore important.

Arsenic and its Oxides

Before beginning the study of the oxidation-reduction of arsenious oxide when combined with a metallic, a study of the properties of arsenic and its oxides was made.

Elemental arsenic is known to exist in three allotropic forms. These were designated by Petersen[1] as: alpha, steel gray, rhombohedral arsenic, formed when the vapor is condensed above 360°; beta, black-gray, amorphous arsenic, formed when the vapor is condensed below 360° [probably not amorphous according to present-day ideas]; gamma, brown, amorphous arsenic, formed by reduction in aqueous solution, greyish-yellow amorphous arsenic, very instable at room temperature. Petersen measured the heats of oxidation of these forms and found alpha arsenic to be the most stable and gamma arsenic the least stable.

Taschtschencko[2] determined the transition temperatures of these modifications by a calorimetric method. The heat evolved on cooling was plotted against the temperatures to which the substance to determine the breaks in the curve. He found that the beta modification can be converted into the alpha modification by sufficiently prolonged heating at 210°.

The vapor density of arsenic was investigated by Biltz and Meyer[3] and by Preuner and Brockmöller.[4] The latter pair found that As_4 is dissociated slightly into As_2 at 600° and that As_2 is dissociated slightly at 1200°. The alpha modification was found to have a vapor pressure of 6 mm. at 400°.

When heated in air, arsenic is oxidized chiefly to arsenious oxide, although Bloch[5] found that some pentoxide is formed direct. By subliming arsenic in a tube closed at one end Regters[6] obtained a yellowish-brown condensate which he believed to be a suboxide. The existence of this oxide has not been proved definitely.

Arsenious oxide and arsenic pentoxide are well known. Several compounds ranging in compositions between these two have been reported; but their existence has not been established satisfactorily. However, Herbst[7] states that a residue of the composition As_2O_4, the tetroxide, is obtained when the pentoxide is heated. The existence of such an oxide might be inferred from the analogy with antimony. No salts of the tetroxide are known.

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[1] Z. physik. Chem., **8**, 607 (1891).
[2] J. Chem. Soc., **121**, 977 (1922).
[3] Z. physik. Chem., **77**, 673 (1911).
[4] Z. physik. Chem., **78**, 129 (1877).
[5] Compt. rend., **149**, 775 (1909).
[6] Z. anorg. Chem., **4**, 401 (1893).
[7] Inaugural Diss. Berne University (1894).

Arsenious oxide condenses in the form of octahedra at temperatures below 250°. At 275° the crystals tend to sinter, and above 315° the condensate is vitreous and transparent. Monoclinic crystals are known to exist; but they are not formed from the vapor under ordinary conditions. Arsenic pentoxide was found by Szarvasy and Messinger[1] to decompose at dull red heat. Auger[2] found that the compound could not be melted without decomposing appreciably. He states that the substance is stable at 400° and decomposes at a dull red heat. Whether or not it can exist in the vapor phase does not appear to have been determined.

General Theory

While the data in regard to the pyrolysis of metallic arsenites appear to be hopelessly contradictory, the general theory is really quite simple. The products depend primarily on two factors: the strength of the base with reference to arsenious oxide; and the reducibility of the base. If the base is not readily reducible and if the dissociation pressure of the arsenite is relatively high, arsenious oxide will sublime off and the base will be left behind. This case will be exactly similar to calcium carbonate. So far as one can judge, the bases falling in this class are the oxides of aluminium, magnesium, zinc, and lead. If the base is not readily reducible and if the dissociation pressure is relatively low, there will be oxidation to arsenate and reduction to metallic arsenic, which may or may not be accompanied by the vaporization of some arsenious oxide. The oxides of sodium, potassium, calcium, and barium fall in this class. If the base is readily reducible and if the dissociation pressure is relatively low, the base will be reduced and some arsenate will be formed. Depending on the absolute value of the dissociation pressure and the degree of reducibility of the base, one may get vaporization of the excess arsenious oxide or oxidation-reduction to arsenate and metallic arsenic. If the metallic arsenic can react with the reduced base, one may get an arsenide or an arsenic-containing product. The oxides belonging in this class include ferric oxide, cupric oxide, and silver oxide. The ferric oxide tends to go to magnetite, the cupric oxide to cuprous oxide, and the silver oxide to metallic silver.

Preparation of Metallic Arsenites

An extensive summary of the preparation of arsenites prior to 1895 is given by Stavenhagen.[3] Since then, the preparation of the arsenites of the heavy metals has been studied by Reichard.[4] Phase-rule studies of the aqueous systems, K_2O, Na_2O, Li_2O with arsenious oxide were made by Schreinemakers and DeBaat;[5] the systems, BaO, CaO, MgO, and PbO with aqueous arsenious oxide, were studied by Story and Anderson;[6] and the systems, MgO, ZnO,

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[1] Ber., **30**, 1344 (1897).
[2] Compt. rend., **134**, 1060 (1902).
[3] J. prakt. Chem., (2) **51**, 18 (1895).
[4] Ber., **30**, 1913 (1897); **31**, 2163 (1898); Chem. Ztg., **26**, 1141 (1902).
[5] Chem. Weekblad, **14**, 262 (1917).
[6] J. Am. Chem. Soc., **46**, 535 (1924).

CuO, FeO, and Fe_2O_3 with aqueous arsenious oxide, were studied by Ruten-ber.[1] The adsorption of arsenious oxide by precipitated ferric oxide and by alumina has been studied by Sen.[2]

In some of these systems, equilibrium is attained only after a long time and it has, therefore, been difficult to determine whether or not stoichiometric compounds exist. It also seems probable that some of the arsenites, thus formed, adsorb arsenious oxide very strongly from solution, so that the prod-uct contains an excess of arsenious oxide. The compounds reported vary widely in composition, probably because of these experimental difficulties.

Three normal acids of arsenious oxide are possible: the ortho, H_3AsO_3; the pyro, $H_4As_2O_5$; and the meta, $HAsO_2$. The corresponding arsenites have been reported as well as many others. Story and Anderson seem to regard the arsenites containing less than arsenious oxide than the meta-arsenite as basic meta-arsenites. From their composition these may be regarded either as basic salts or as hydrated normal salts. Thus $Ca(OH)AsO_2$ has the same composition as $Ca_2As_2O_5.H_2O$, and $Na_3(OH)_2AsO_2$ has the same composition as $Na_2AsO_3.H_2O$. On the other hand, Rutenber concluded that ortho-arsenites are formed with cupric, zinc, and ferrous oxides. He did not discover any pyro-arsenites.

The following general methods have been used by me in the preparation of arsenites:—

1. Reaction of arsenious oxide with the metallic oxide or hydroxide (synthesis).

2. Reaction of a soluble arsenite with a soluble salt of the metal to form an insoluble arsenite (metathesis).

The first of these methods should produce a purer product, as no foreign substance except water is introduced. It was used, therefore, whenever possible. However, previous investigators have only succeeded in a few in-stances in producing pure compounds by this method, probably due to the slow rate of reaction. There is also danger of partial oxidation of the ar-senious oxide at the boiling temperature.

Precipitation methods (metathesis) were found to give arsenites of definite composition only in a few cases and these were so soluble that frequently the precipitates could not be washed without considerable loss. The method generally used was to wash with cold water until one cc. of the wash-water showed a constant titre with standard iodine solution. This was taken to indicate that the excess arsenious oxide had been removed and that the residue should presumably consist of pure arsenite. This conclusion was not always justifiable. In some instances the discrepancy could be explained as due to hydrolysis, and in other cases as due to very strong adsorption of arsenious oxide by the arsenite.

Kahlbaum's arsenious oxide (ph.G.) was tested by the method of Chapin[3] and found to contain appreciable quantities of sulphide but no antimony or

[1] Cornell Thesis (1929).

[2] J. Phys. Chem., **31**, 419 (1927).

[3] J. Ind. Eng. Chem., **10**, 522 (1918).

heavy metals. It also left a very small non-volatile residue at red heat. When heated in a lipless beaker covered with a watch-glass on an electrically-heated hot plate, a red sublimate appeared at first, presumably the disulphide, As_2S_2. When this was removed and a clean watch-glass substituted, colorless octahedral crystals were obtained, which gave no test for sulphide or for antimony, and which left no residue when resublimed by the same method or when heated to a red heat. It was therefore considered to be sufficiently pure for use in the preparation of arsenites.

On evaporating down solutions of alkaline arsenites, a crystalline residue was obtained only with potassium and lithium; the sodium arsenite could not be made to crystallize. The lithium salt was very close to the meta-arsenite in composition; but the potassium salt could not be dehydrated completely without decomposition, so that it may have been a hydrated meta-arsenite. On adding alcohol to the solutions, they became cloudy; but the arsenite formed would not settle and could not be filtered.

When cold, aqueous, arsenious oxide solutions were added to solutions of the hydroxides of the alkaline earths; in cold water, no precipitates were obtained with barium and strontium hydroxides. With lime water in excess, a precipitate was obtained containing three percent more arsenious oxide than the ortho-arsenite. When the arsenious oxide was in excess, the meta-arsenite of calcium was obtained. With barium hydroxide, precipitates were obtained only from the hot concentrated solutions. When the hydroxide was in excess, the precipitate contained four percent more arsenious oxide than the ortho-arsenite; when the arsenious oxide was in excess, the precipitate contained about five percent more arsenious oxide than the meta-arsenite.

On prolonged contact with aqueous arsenious oxide, strontium hydroxide gave a substance that was intermediate in composition between the meta-arsenite and the pyro-arsenite and contained some water. It could not be dehydrated completely without decomposition. The arsenious oxide content could not be increased by allowing to stand for five months. Stavenhagen did not succeed in preparing a strontium arsenite of definite composition.

In contact with aqueous arsenious oxide, magnesium oxide was found to give a substance slightly in excess of the amount required for the ortho-arsenite. This did not increase on standing two months longer. Story and Anderson, and Rutenber found no arsenite of magnesium.

Zinc oxide formed the ortho-arsenite from aqueous arsenious oxide in a few days and the meta-arsenite was formed after three weeks of contact. These compounds were obtained by Rutenber and appear to be about the most easily prepared arsenites known.

The substance obtained on prolonged contact of precipitated lead oxide with aqueous arsenious oxide was found to contain only forty-one percent arsenious oxide, whereas the meta-arsenite was obtained by Story and Anderson and requires forty-seven percent. As in the case of the strontia, the lead oxide apparently refused to take up any more arsenious oxide.

When precipitated alumina was dried at 140°, it was found to retain about twenty percent of water. When the undried gelatinous substance was placed

in aqueous arsenious oxide and dried at 140°, it was found to contain about forty percent alumina, forty percent arsenious oxide, and twenty percent water. On the dry basis this is equivalent to fifty percent arsenious oxide. The ortho-arsenite requires sixty-six percent.

It was difficult to determine the amount of arsenious oxide taken up by ferric oxide; but the loss of weight on heating to redness indicates that ferric ortho-arsenite was formed.

Heating Arsenites in Air

Simon[1] heated calcium pyro-arsenite, $(CaO)_2.As_2O_3$, and calcium meta-arsenite, $CaO.As_2O_3$, in the air and found that the loss of weight was always less than that calculated on the assumption that four atoms of elemental arsenic are formed and driven off for every three molecules of arsenious oxide oxidized to the pentoxide and combined with the calcium oxide, as illustrated by the equations:—

(1) $5 As_2O_3 = As_4 + 3 As_2O_5$
(2) $5 Ca_2As_2O_5 = 10 CaO + 5 As_2O_3 = As_4 + 10 CaO + 3 As_2O_5$
(3) $5 CaAs_2O_4 = 5 CaO + 5 As_2O_3 = As_4 + 5 CaO + 3 As_2O_5$
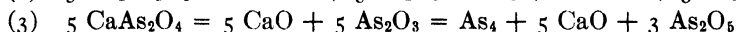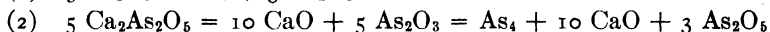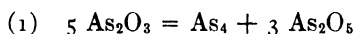
This means that some oxidation is caused by the air. Since the ratio $3 As_2O_5/5 As_2O_3 = 0.6970$, a higher ratio means an oxidation by air, while a lower ratio means the volatilization of some As_2O_3 or the decomposition of some As_2O_5.

Various arsenites were heated to constant weight in porcelain crucibles over a Bunsen burner and the arsenious oxide in the residue determined by titration with iodine. In most cases, the amount of arsenious oxide was

<div align="center">TABLE I</div>

A	B	C	D	E	F
CaO	77.9	1:1	76.3	56.8	2.62:1
CaO	77.9	1:1	76.3	61.2	2.30:1
CaO	77.9	1:1	76.3	58.8	2.45:1
CaO	60.0	2.33:1	81.8	91.50	2.98:1
CaO	60.0	2.33:1	81.9	89.42	3.31:1
SrO	56.45	1.48:1	83.2	67.74	3.88:1
SrO	56.45	1.48:1	83.2	66.92	4.0:1
BaO	63.37	0.745:1	81.1	51.21	4.56:1
BaO	69.37	0.745:1	86.1	49.34	4.10:1
Na₂O	89.35	0.376:1	72.8	33.26	1.77:1
Na₂O	89.35	0.376:1	72.8	29.72	2.18:1
MgO	77.13	1.43:1	76.6	28.23	24.3:1
PbO	37.70	1.45:1	86.6	77.39	4.26:1
ZnO	44.77	3:1	86.2	93.48	4.10:1

A = basic oxide; B = percent As_2O_3; C = mol ratio basic oxide to As_2O_3; D = percentage residue calculated on assumption that reaction proceeds normally; E = percentage residue found; F = mol ratio basic oxide to As_2O_5.

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[1] Pogg. Ann., **40**, 417 (1837).

negligible and was not considered in the calculations. If all of the arsenious oxide should volatilize, the weight of the residue should be equal to the weight of the basic oxide in the original sample and the percentage weight of the residue would be equal to the percentage of basic oxide. In most cases the residue weighed considerably more than the pure basic oxide would, indicating that appreciable amounts of arsenite had formed. This was confirmed by a qualitative test with potassium iodide on a solution of the residue in hydrochloric acid.

The experimental data are given in Table I.

From these data it is possible to draw the following conclusions:—

(1)   Calcium meta-arsenite does not react according to equation (3) at the temperature reached when heating with a Bunsen burner. It loses more weight and the residue contains more lime than predicted by this equation. It is probable that Simon did not heat to so high a temperature or for so long a time; he apparently did not determine whether the reaction had gone to completion.

(2)   A substance containing somewhat less arsenious oxide than calcium pyro-arsenite loses less weight than calculated from equation (1) and the residue approximates the composition of calcium ortho-arsenate, containing much more arsenic pentoxide than is predicted by equation (2). This undoubtedly means oxidation by the air.

(3)   Strontium arsenite, of a composition between those of the pyro-and meta-arsenites, left a residue much smaller than calculated, although strontium oxide might be expected to be more reactive than calcium oxide, as it is more basic. This arsenite was found to contain some combined water, probably combined with the strontia as hydroxide, and this may have interfered with the reaction.

(4)   Barium arsenite containing more arsenious oxide than the meta-arsenite was found to leave a residue smaller than that calculated and this difference is much less than the corresponding difference for the calcium meta-arsenite. However, this salt apparently contains a small amount of combined water also and Stavenhagen[1] regards it as an acid salt.

(5)   Sodium arsenite containing a large excess of arsenious oxide over the meta-arsenite left residues approximating the composition of sodium pyro-arsenate. This indicates that sodium oxide is much more reactive than barium oxide, although this difference may be due to the fact that sodium arsenite melted before much arsenious oxide vaporized from it. The liquid may have held more arsenious oxide in solution until it reacted.

(6)   Magnesium oxide was found to retain much less arsenic pentoxide than any of the substances investigated, differing very markedly from calcium oxide in this respect. Apparently it is much less basic.

(7)   Arsenite of lead, between the meta and pyro in composition lost much less weight than the magnesium compound of closely corresponding composition, and much less than might be expected from the position of this element in the periodic table. The fact that the substance melted may account for this.

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[1] J. prakt. Chem., (2) **51**, 17 (1895).

(8) Zinc ortho-arsenite left more residue than calculated, showing that some oxidation by air took place. This was due to some extent to the large proportion of zinc oxide in the compound; but it appears to be the most active element studied, next to calcium, and it is much more active than might be expected from its weakly basic, in fact amphoteric, nature.

Going back to the behavior of calcium meta-arsenite when heated in air, there are two ways of accounting for the relatively small amount of residue. One is that some arsenious oxide vaporizes off. The other and more probable one is that calcium meta-arsenate may be instable at a bright red heat and may decompose into calcium ortho-arsenate or into a mixture of calcium ortho-arsenate and pyro-arsenate. The data in the literature are contradictory.

Bloxam[1] prepared calcium meta-arsenate by dissolving calcium carbonate and arsenious oxide in nitric acid, evaporating to dryness and igniting the residue. This indicates that the compound is stable at a bright red heat. However, Mitscherlich[2] heated an arsenate of calcium, probably the pyro-arsenate, in a porcelain tube in a stream of nitrogen and found it to be almost completely decomposed at a bright red heat.

To determine whether or not the meta- and pyro-arsenates can be formed from calcium oxide and arsenious oxide in presence of air, at bright red heat, the amount of arsenic pentoxide taken by a given amount of calcium oxide was determined.

Chemically pure calcium oxide was heated to constant weight in a porcelain boat in a silica combustion tube heated by means of Bunsen burners. A boat containing arsenious oxide was then placed in the tube and the vaporized arsenious oxide drawn over the calcium oxide by means of a stream of air. This was done fourteen times and the boat containing calcium oxide was weighed after each addition of arsenious oxide. The data are given in Table II.

TABLE II

Increase in Weight of Calcium Oxide when reacting with Arsenious Oxide and Oxygen. Weight of CaO = 1.9386 g.

No.	Gain in Weight	Percent Gain	No.	Gain in Weight	Percent Gain
1	2.4166 g	131.0	8	0.0604 g.	3.3
2	0.2214	12.0	9	0.0210	1.2
3	0.0956	5.2	10	0.0192	1.0
4	0.0206	1.1	11	0.0032	0.2
5	0.0508	2.8	12	0.0108	0.6
6	0.0263	1.4	13	0.0284	1.5
7	0.0317	1.7	14	0.0030	0.2

The final weight of the product was 4.8824 g. The percentage calcium oxide was 37.6. Since there was very little arsenious oxide in the product, the percentage of arsenic pentoxide was very close to 62.4. After the first run the

[1] Chem. News, 54, 193 (1886).
[2] Ann. Chim. Phys., (6) 27, 22 (1892).

percentage of arsenic pentoxide was 56.7 which is not much below the theoretical value of 57.9 for calcium ortho-arsenate. It seems probable that the reaction takes place rapidly to form the ortho-arsenate, after which the final equilibrium is approached much more slowly. The final product seems to be an equimolecular mixture of the ortho- and pyro-arsenates.

When there is an excess of lime the residue is greater than the theoretical. This phenomenon occurred only with calcium and zinc oxides. The great activity of calcium oxide, and possibly also that of zinc oxide, might perhaps be explained by an experiment done by H. B. Baker.[1] Silica tubes containing a mixture of hydrogen and nitrous oxide dried to such an extent that the moisture was only a few milligrams to a million liters, were heated in a resistance furnace in pairs. One tube contained lime and the other powdered Jena glass. When the combining temperature was reached, the rate of union in the lime tube was five times that in the tube containing the powdered glass. After fifteen minutes heating, when a large amount of water had been formed from the reaction, the reaction velocities became the same. Baker regards this as due to the calcium oxide causing gaseous ionization, which accelerates the reaction by furnishing nuclei for the condensation of the water vapor. He found radio-active substances to have a much greater effect than calcium oxide.

Heating Arsenites in an Inert Atmosphere

In order to provide a method of heating sealed glass tubes uniformly and without danger from flying glass in case of explosion, electric furnaces were constructed as follows:—

A section of $1\frac{1}{4}''$ iron pipe about 8" long and threaded at both ends was fitted with an asbestos collar at each end and the pipe surface in between was covered with alundum cement to a thickness of about $\frac{1}{4}''$. No. 20 gauge chromel wire was then threaded through a small hole in the asbestos and wound spirally on the surface of the alundum cement. The wire was then covered with a second layer of alundum cement, and this was covered with asbestos cement to a thickness of several inches. One end of the pipe was then closed with a pipe-cap and this was also covered with a thick layer of asbestos cement. The other end was provided with a cap with a hole about $\frac{1}{2}''$ in diameter drilled at one side for the insertion of a thermometer or thermocouple. The furnace was placed in a vertical position with the removable cap uppermost. The bottom of the pipe was filled with asbestos fibre to prevent the loss of heat through the lower end and to prevent breakage of the sealed tubes by striking the bottom.

The furnaces were connected to alternating current outlets through lamp banks. When tungsten lamps were used, the daily variation in temperature was much less than with carbon lamps. This is probably due to the negative temperature coefficient of resistance of carbon, which would permit less current to flow through the filament when the temperature is decreased by a decrease in the power, and more when there is an increase.

[1] J. Chem. Soc., **1928**, 1054.

Since the carbon filament lamps caused a greater variation in the temperature than tungsten lamps when connected in series with the furnace, it seemed probable that they would decrease in variation if connected in parallel, since they would by-pass more current as their temperature increased, and less when it decreased. It was found that when six carbon lamps of 120 watts were connected across the terminals of a furnace that had previously shown a maximum temperature variation of 22°, it showed a temperature variation of only 13° over a much greater length of time. Another furnace that had varied as much as 17° formerly, when connected to two 120-watt carbon lamps in a similar manner, varied only 11°. These experiments are not regarded as conclusive; but they give promise of a method of regulating temperatures without the use of the elaborate equipment required by other methods.[1]

To determine if air can be displaced from a tube filled with nitrogen, the following experiment was performed:—

Two pyrex tubes were sealed off and rounded at one end. Some bright copper wire was placed in the bottom of each, and the tubes were then drawn out to form a narrow constriction three or four inches from the closed end. Nitrogen from a small cylinder was passed into one of these through a small pyrex tube inserted through the constriction and held in place by means of an asbestos plug. The nitrogen was allowed to flow for several minutes, the tube was then withdrawn beyond the constriction and the copper wire sealed off with the nitrogen still flowing at the point of sealing. The other tube was sealed off with the air which it contained.

Both tubes were heated in the furnaces previously described for about twelve hours at 270°-300°. The copper sealed off in nitrogen remained completely unchanged, whereas that sealed off in air had turned completely black. This was taken as evidence that atmospheric oxygen can be displaced by this method, although, of course, adsorbed air on the surface of fine powders may not be so easily displaced. The method dispenses with the vacuum pump and makes stronger seals possible.

The method of displacing the air in the tube as outlined above, was used for the study of the thermal decomposition of arsenites in the absence of oxygen. To insure the complete absence of oxygen, the nitrogen was bubbled through a wash-bottle filled with potassium pyrogallate. The substance to be examined and the tube in which it was sealed were dried at about 150° for the purpose of driving off adsorbed air. A higher temperature would cause decomposition or oxidation of some of the substances.

The amount of arsenious oxide in the original sample was determined by titrating with iodine solution standardized against pure arsenious oxide. After sealing off in nitrogen and heating for various lengths of time, the tube was cracked open and the residue in the bottom titrated again. When a sublimate of elemental arsenic or arsenious oxide was formed in the upper end of the tube the amount of this was determined by weighing this part of the tube,

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[1] See Adams: J. Optical Soc. America, **9**, 599 (1924).

heating to drive off the sublimate, and weighing again. The amount of arsenious oxide oxidized was estimated from the difference in the two titrations, and could be compared with the amount of sublimate.

A weighed sample of copper ortho-arsenite, $Cu_3(AsO_3)_2$, prepared by Mr. Rutenber, was sealed in nitrogen by the method described above and heated at $370°$-$387°$ for about eight days. At the end of this time the green substance had turned to an orange-red color, and a small amount of vitreous arsenious oxide condensed in the upper part of the tube when it cooled. The tube was cracked open by making a file mark around it and touching this with a white-hot piece of pyrex. The upper portion of the tube was weighed, heated to redness, and weighed again, the weight of arsenious oxide being determined by difference. This was found to be 20.8 percent of the weight of the sample, while the total arsenious oxide in the original sample was 45.33 percent.

The residue, the red substance formed in the bottom of the tube, was found to dissolve readily in hydrochloric acid and in ammonia. When the ammoniacal solution was acidified with acetic acid, potassium iodide produced a white precipitate, showing that a cuprous salt was present. When silver nitrate was added to the acetic acid solution, a brown precipitate of silver arsenate was formed.

A mixture of cupric oxide (Baker's analyzed) and of arsenious oxide (purified by sublimation) containing the two oxides in the same proportions, (54.17 and 45.33 percent) as in copper ortho-arsenite was sealed in nitrogen and heated at $337°$-$348°$ for twenty-five days. The residue, after heating, had the same appearance as in the preceding experiment, and there was also formed a vitreous condensate which caused the tube to crack when cooled. The fragments were collected and the arsenious oxide determined by dissolving in sodium hydroxide solution, neutralizing with acid, and titrating with iodine in the presence of an excess of bicarbonate. The percentage of arsenious oxide thus formed was 21.8, very close to the value obtained in the preceding experiment. If we assume, as seems probable, that all of the arsenious oxide that did not react condensed in the upper portion of the tube, something over one-half of the arsenious oxide was oxidized to arsenate. Since there is enough cupric oxide in cupric-ortho arsenite to oxidize three-quarters of the arsenious oxide, and only about fifty-four percent was oxidized, the amount of arsenious oxide oxidized to arsenic pentoxide is only a little over seventy percent of the amount theoretically possible. Consequently some of the cupric arsenite lost arsenious oxide direct without any corresponding reduction of the cupric oxide.

Silver ortho-arsenite was prepared by adding a solution of arsenious oxide in sodium hydroxide to an equivalent quantity of silver nitrate. The yellow precipitate turned black on drying at $150°$. The substance was analyzed by dissolving in dilute nitric acid, precipitating, and weighing the silver as silver chloride. The filtrate was neutralized and titrated for arsenious oxide in presence of bicarbonate. The silver oxide came out 77.63 and 77.72 percent and the arsenious oxide 19.82 and 19.72 percent. The low value for arsenious oxide was probably due to partial oxidation by nitric acid while dissolving the

samples, because silver ortho-arsenite calls for 77.84 percent silver oxide and 22.16 percent arsenious oxide. In the following experiments it is assumed that the salt contained the theoretical amounts of the two oxides.

A weighed sample was sealed in nitrogen and heated for ten days at 378°-402°. The condensate of vitreous arsenious oxide cracked the tube as it cooled in such a way that the fragments could not be collected. The residue had sintered to a brownish-black lump which was found to contain particles of silver mixed with silver arsenate. The silver arsenate was dissolved in ammonia and the metallic silver collected on a filter paper, ignited and weighed. It was then dissolved in nitric acid and titrated with thiocyanate solution. The silver was thus found to be 98.97 and 96.51 percent pure and to constitute 31.2 and 30.8 percent of the weights of the samples. The silver in solution was precipitated as silver chloride and calculated as 48.96 and 48.84 percent silver oxide. The filtrate was neutralized and titrated with iodine in the presence of bicarbonate. The volume of iodine taken was the same as for a blank on the ammonia used, and therefore no appreciable amount of arsenious oxide was present. The content of arsenic pentoxide was therefore about 20.1 percent, by difference.

Another sample of the silver ortho-arsenite was heated at 206°-218° for fourteen days. A condensate of octahedral arsenious oxide formed in the upper part of the tube as it cooled, and the residue in the bottom of the tube had about the same appearance as in the preceding experiment. The tube was opened by the method used previously and the arsenious oxide in the upper portion determined to be 6.7 percent of the original weight of the sample. The residue was found to contain 34.6 and 35.2 percent metallic silver, 46.5 and 46.9 percent silver oxide, and about 18.4 percent arsenic pentoxide, the last by difference.

The reaction probably takes place essentially according to the equation

$$2 \, Ag_2O + As_2O_3 = 4 \, Ag + As_2O_5.$$
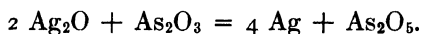
Since silver ortho-arsenite contains three molecules of silver oxide to one of arsenious oxide, there is enough silver oxide to oxidize all the arsenious oxide, in which case the residue should contain silver oxide and arsenic pentoxide in equivalent amounts. Actually the molecular ratio was 2.43 in the first case and 2.51 in the second case. This means that the composition lies about half-way between the ortho- and the pyro-arsenate, which is substantially what was found with lime. Since the amount of arsenate is less than the calculated amount, some arsenious oxide must have vaporized, as was shown experimentally to be the case.

Another sample of silver ortho-arsenite heated in nitrogen for thirty-six hours at 116°-119° showed no sign of change. The temperature was increased gradually by about ten degrees at a time. A condensate of arsenious oxide appeared at 149°-156°, and the residue appeared to turn slightly brown. The initial temperature of the reaction is therefore about 150°.

Potassium arsenite was prepared by dissolving arsenious oxide in potassium hydroxide solution and evaporating until crystals appeared. The liquid was

then decanted off and more water added. This solution was evaporated to dryness and the residue dried at 110°. When heated in a test-tube over the Bunsen burner, the substance turned black, giving off water vapor and the garlic-like odor attributed to metallic arsenic, showing that the substance undergoes oxidation-reduction readily. Qualitative tests showed the presence of some arsenate and carbonate. Titration with iodine gave 56.24 and 56.55 percent arsenious oxide, average 56.4. The formula for the meta-arsenite requires 67.95 percent. This substance may be the meta-arsenate with large amounts of water, arsenate, and carbonate. It was found impossible to dry the substance completely as it turned slightly dark at 150°.

A weighed sample of this substance was heated in nitrogen for sixteen days at 382°-401°. At the end of this time it had turned quite dark; but no condensate appeared on cooling. Samples of the product were dissolved in water, and the black portion, which did not dissolve, was collected on Gooch crucibles and weighed. It was found to be completely volatile when heated to redness, and was apparently elemental arsenic. The losses of weight on heating were 0.37 and 0.26 percent, average 0.32. The solution was neutralized with acid and titrated with iodine in presence of bicarbonate. The percentage of arsenious oxide found was 52.1 and 51.8 percent, average 52.0. This is a decrease of 4.4 percent from the amount originally present.

If we assume that the reaction takes place according to the equation

$$5 \text{ As}_2\text{O}_3 = \text{As}_4 + 3 \text{ As}_2\text{O}_5,$$
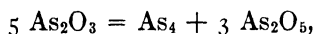
there should have been 1.3 per cent metallic arsenic instead of the 0.32 percent actually found. It is probable that there was oxidation by water vapor. This is the more likely because Bloxam[1] has shown that alkaline arsenites can be oxidized by water vapor.

Barium arsenite was prepared by adding crystals of arsenious oxide purified by sublimation) to baryta water and heating gently. The residue, dried at 140°, was found by titration with iodine to contain 34.9 and 34.5 percent arsenious oxide and to be free from arsenate. The formula for barium ortho-arsenite, $\text{Ba}_3(\text{AsO}_3)_2$ calls for 30.0 percent arsenious oxide.

A weighted quantity of this substance was heated at 388°-393° for ten days. The residue turned yellowish-brown, and the grey modification of metallic arsenic condensed at the top of the tube when it was removed from the furnace. This condensate was vaporized off and the loss of weight determined. It was 5.5 percent of the original weight. The residue was found to dissolve partially in dilute hydrochloric acid, leaving a brownish residue which was assumed to be metallic arsenic. In both experiments it amounted to 0.85 percent of the original weight of the sample. The filtrate was neutralized and titrated with iodine, showing 14.89 and 16.46 percent of arsenious oxide. The decrease in arsenious oxide is $35.2 - 14.7 = 20.5$ percent, while the metallic arsenic is equivalent to 21.0 percent, which is probably identical within the limit of experimental error.

[1] J. Chem. Soc., **15**, 281 (1862).

Calcium meta-arsenite was prepared by boiling crystals of arsenious oxide with lime water. When dried at 100°, it was found by titration with iodine to contain 77.57 and 77.31 percent arsenious oxide, very close to the 77.93 percent calculated for $Ca(AsO_2)_2$. A weighed quantity was sealed in nitrogen and heated at 354°-357° for 53 hours. When examined at the end of this time, the arsenite had turned brown and a small amount of metallic arsenic had condensed at the top of the tube on cooling. The tube was cracked open, treated as before, and the total metallic arsenic found to be 0.05 percent. The acid filtrated was neutralized and titrated with iodine. The amount of arsenious oxide found was 77.8 and 70.2 percent. Since this is more than we started with, the original sample must have contained water which was lost on heating. The arsenic pentoxide was slightly in excess of the theoretical, showing that there had probably been some oxidation by water vapor. The essential reaction is oxidation-reduction.

Arsenites containing more Arsenious Oxide than the Meta-arsenites

Bloxam[1] found that, when potassium carbonate and sodium carbonate were saturated with arsenious oxide, the residue left on driving off the water contained two molecules of arsenious oxide combined with one molecule of the respective basic oxides. These bi-arsenites, as he called them, are probably formed by the dehydration of the acid meta-arsenites, $KH(AsO_2)_2$ and $NaH(AsO_2)_2$. They can be fused at temperatures at which the vapor pressure of arsenious oxide is high without liberating this anhydride, which indicates that they do not contain free arsenious oxide. However, Bloxam found that, in the presence of moisture, some arsenic is liberated on fusion and some arsenate is formed, even in an atmosphere of carbon dioxide. This suggests that arsenious oxide undergoes some oxidation-reduction when in combination with alkali oxides, even when the relative amount of the basic oxide is relatively small. The following experiments were made to determine to what extent the reaction takes place in such compounds.

A commercial sodium arsenite (J. T. Baker's) was titrated with iodine and found to contain 89.50 and 89.13 percent arsenious oxide, as compared with 70.71 percent for sodium meta-arsenite and 86.5 percent for sodium di-arsenite, $Na_2O.2As_2O_3$. A weighed sample was sealed in nitrogen and heated for six days at 339°-353°. A small, transparent, vitreous condensate was formed on cooling, and there was no discoloration of the residue. Titration of the residue with iodine indicated a decrease of only 0.88 percent arsenious oxide, showing that only a small amount vaporized.

Another sample of the same substance was heated at 362°-387° for 4.5 days. There was no discoloration of the residue, indicating that no elemental arsenic was formed. The weight of the transparent condensate was 0.66 percent of the weight of the original sample. Titration of the residue indicated a loss of 1.34 percent arsenious oxide, so there was probably a small amount of oxidation to arsenate without the formation of metallic arsenic. This may have been due to adsorbed air or to small amounts of moisture.

[1] J. Chem. Soc., **15**, 284 (1862).

Barium arsenite, prepared by adding an excess of a solution of arsenious oxide to baryta water, was dried at 140°, and found to contain 63.18 and 63.37 percent arsenious oxide as compared with 56.34 percent for barium meta-arsenite, $Ba(AsO_2)_2$. Bloxam[1] obtained an arsenite containing only slightly less arsenious oxide by precipitating barium chloride with sesqui-arsenite of soda, $2Na_2O.3As_2O_3$, which also contained more arsenious oxide than sodium meta-arsenite. Story and Anderson[2] appear to have prepared a hydrated sesqui-arsenite of barium in their study of the system, $BaO-As_2O_3-H_2O$.

A weighed amount of the substance prepared as described was sealed in nitrogen and heated at 312°-317° for twenty-four hours. A slight, transparent, vitreous condensate appeared. The heating was continued at 316°-323° for four days without any apparent, further change. The temperature was raised to 402°-410° and held there for four days. A small amount of a black condensate appeared when the tube cooled. Apparently a straight thermal dissociation takes place at the lower temperature and oxidation-reduction does not occur until an appreciable amount of the arsenious oxide is driven off.

The amount of arsenious oxide at the top of the tube was only 0.3 percent and the amount of elemental arsenic was so small that it could not be determined. The residue dissolved practically completely in hydrochloric acid and gave only a slight color with potassium iodide, indicating that oxidation-reduction took place only to a negligible extent.

Crystalline strontium hydroxide was allowed to stand in contact with a supersaturated solution of arsenious oxide until there was no further decrease in the titre of the solution. The solid was then collected on a filter and dried at 105°. Titration with iodine gave 73.99 and 71.4 percent arsenious oxide, which indicates that the substance is the sesqui-arsenate, $2SrO.3As_2O_3$, which contains 74.13 percent arsenious oxide.

A weighed quantity of this substance was sealed in nitrogen and heated for five days at 373°-385°. A vitreous, transparent condensate was formed on cooling with a few small crystals of elemental arsenic. The residue had turned dark gray. The arsenious oxide sublimed off was 29 percent of the original weight and the decrease in arsenious oxide as shown by titration was 28.6 percent. The total amount of metallic arsenic was only 0.32 and 0.28 percent. This corresponds to about 0.9 percent arsenious oxide. The residue contained 62.5 and 63.1 percent arsenious oxide, rather less than the 65.63 percent corresponding to the meta-arsenite. Much more arsenious oxide vaporized than was the case with sodium and barium oxides. This may have been due to the presence of some free arsenious oxide in the samples.

To make calcium di-arsenite a saturated solution of arsenious oxide was mixed with lime water and evaporated slowly until a precipitate appeared. This was filtered off and found to contain 89.71 and 89.92 percent arsenious oxide as compared with 87.6 percent in calcium di-arsenite, $CaO(As_2O_3)_2$. Some of this substance was sealed in nitrogen and heated for 18 hours at 350°-360°. The residue turned gray and a transparent, vitreous condensate

[1] J. Chem. Soc., 15, 294 (1862).

[2] J. Am. Chem. Soc., 46, 535 (1924).

appeared in the top of the tube on cooling. The tube cracked so much that the amount of this condensate could not be determined. Titration of the residue with iodine gave 87.99 and 88.30 percent arsenious oxide. The Gooch-Browning titration showed about 0.2 percent arsenic pentoxide, corresponding to about 0.1 percent metallic arsenic and about 0.3 percent arsenious oxide.

The decrease in arsenious oxide content is 1.67 percent, 0.3 of which can be attributed to oxidation-reduction, leaving 1.3 percent as the arsenious oxide driven off. This is not as great as the difference between the arsenious oxide content of the substance and that of the di-arsenite, showing that the excess above the di-arsenite, as in the sodium compound, was not free to vaporize as arsenious oxide, or at least did not do so in the rather short time of heating.

The results of these experiments are summarized in Table III.

<div align="center">TABLE III</div>

Basic Oxide	Mol Ratio Basic Oxide to As_2O_3	Decrease in As_2O_3 %	As_2O_3 Condensed %	Metallic Arsenic %	Temperature
Na_2O	0.38	1.34	0.66	None	362°-387°
BaO	0.75		0.30	Trace	402°-410°
SrO	0.67	29.5	28.6	0.23	373°-385°
CaO	0.40	1.7	1.3	0.1	350°-360°

All of the arsenites which contain more arsenious oxide than the meta-arsenite, with the exception of the strontium salt, lose only small quantities of arsenious oxide when heated in closed tubes at temperatures at which this anhydride has an appreciable vapor pressure. The amount of elemental arsenic, due to oxidation-reduction is likewise small.

The thermal stability of these substances indicates that (with the exception of the strontium salt) they are true compounds and not meta-arsenites containing an excess of uncombined arsenious oxide. Di-arsenites may be regarded as analogous to dichromates and tetraborates:—thus sodium di-arsenite, $Na_2O.(As_2O_3)_2$, can be written $Na_2As_4O_7$ or $(NaAsO_2)_2.As_2O_3$, completely analogous to the formula for borax. The existence of these di-arsenites or tetra-arsenites stable toward heat is probably related to the weakly acid character of arsenious anhydride, as boric acid is also very weak, and a strong base may be expected to form stable compounds with an excess of a weak acid.

The data for the calcium and sodium salts indicate that arsenious oxide may be retained in combination even when present in excess of the theoretical amounts for the di-arsenites. This failure of the excess arsenious oxide to vaporize may be due to the slow rate of evaporation of melted arsenious oxide observed by Tammann and Bätz,[1] or to a tendency of arsenious oxide to disso've in the di-arsenite.

[1] Z. anorg. allgem. Chem., 156, 94 (1926).

The fact that oxidation-reduction took place to so slight an extent in these substances indicates that this reaction is dependent upon the presence of a basic oxide. When the basic oxide is so saturated with the acid anhydride as to lose its basic character, it is to be expected that the reaction will no longer take place. The comparison of the two barium arsenites studied is particularly striking in this connection. The data show that the substance containing about 35.2 percent arsenious oxide undergoes oxidation-reduction at 380°-393° to such an extent that about 58.5 percent of the arsenious oxide present is decomposed, whereas the substance containing 63.5 percent arsenious oxide showed apparently only a small thermal dissociation into its anhydrides and only a trace of metallic arsenic to indicate oxidation-reduction.

Determination of Initial Temperature of Reaction

The substance was sealed off in a glass tube about 10 cm. long, as described previously, in an atmosphere of nitrogen at atmospheric pressure. This means about two atmospheres pressure when heated to around 300°. It was found that Jena glass tubes were quite apt to blow up if handled with crucible tongs when hot, and the tubes were therefore placed in spirals of nichrome wire, by which they were lifted from the furnace without coming in contact with cold metal. To determine the initial temperature of reaction, the tubes, enclosed in the spiral of nichrome wire, were placed in the furnace at about 200°, heated at that temperature for about twenty-four hours, removed from the furnace and examined. They were then allowed to cool to room temperature and were examined again. By this method the presence of a condensing vapor in the tube can be detected. If no change occurred, the temperature was raised about ten degrees and the experiment repeated until a change could be detected.

A commercial sample of potassium arsenite (Vernier and Hobein) dried at 150° was found to contain 57.05 and 57.57 percent arsenious oxide with appreciable quantities of arsenite, water, and carbon dioxide. The formula for the meta-arsenite requires 67.75 percent arsenious oxide, so this might be meta-arsenite with a large amount of impurities. A sample of this substance was sealed in nitrogen and heated as described. A slight darkening was first noticed at 313°-317° and there was no condensate. When heated to 365°, the substance became only slightly darker, and no vaporization of the arsenic took place, although some water condensed on cooling. The presence of water vapor may interfere with the accurate determination of the initial temperature of reacting with the arsenic formed. The initial temperature of the oxidation-reduction of this substance is placed tentatively at 313°-317°.

Calcium meta-arsenite, prepared by the interaction of calcium oxide with an aqueous solution of arsenious oxide, was found on analysis to contain about 75.74 percent arsenious oxide, as compared with 77.92 percent for calcium meta-arsenite, $Ca(AsO_2)_2$. The lime contained some impurities, which may account for this difference. When sealed in nitrogen and heated

as described, it became slightly discolored at 360°, and a very small yellow sublimate appeared. It seems probable that the yellow color is due to some interaction of the arsenic with water vapor. The solid hydrides, $(AsH)_n$ and $(As_2H)_n$ may have this color under certain conditions; but, as they are known to be instable at 200°, the color may be due to the brown suboxide, the existence of which has been disputed. There is a yellow modification of elemental arsenic; but this is known to be very instable at ordinary temperatures.

A commercial sample of zinc ortho-arsenite (Häen) was found by titration with iodine to contain 42.27 and 42.48 percent arsenious oxide, as compared with 44.77 percent in $Zn_3(AsO_2)_2$. The substance gave a positive test for arsenite. It may be ortho-arsenite that has undergone some oxidation. This substance, when sealed in nitrogen, gave a condensate of octahedral crystals (arsenious oxide) when cooled from 510° and a small amount of a black condensate appeared when the temperature reached 549°.

The experiment was repeated, using a zinc arsenite prepared by the reaction of zinc oxide with aqueous arsenious oxide and containing 45.14 and 44.83 percent arsenious oxide, a little above the composition of the ortho-arsenite, and no arsenate. With this substance octahedral crystals appeared at 500°-508° after 24 hours. When heated 24 hours longer at the same temperature, a black condensate appeared, indicating that the oxidation-reduction reaction takes place with time. The heating was continued for 48 hours at the same temperature without changing the nature of these condensates.

The difference in the initial reaction temperatures of these two samples of zinc arsenite indicate that the initial dissociation temperature of the substance into its components is lowered by increasing the arsenious oxide content, and that the initial temperature of the oxidation-reduction reaction is raised by appreciable quantities of arsenate, a product of this reaction.

A substance prepared by the interaction of pure, precipitated alumina with aqueous arsenious oxide, when dried at 150°, was found to contain 31.52 and 31.58 percent arsenious oxide on titration with iodine. However, when samples were heated to redness in porcelain crucibles, they were found to lose between 31 and 46 percent of their weights, and the residues were found still to contain appreciable quantities of the oxides of arsenic. The results of the titrations are probably low due to the adsorption of arsenious oxide by the alumina precipitated by the bicarbonate of soda used. The substance probably contains about fifty percent arsenious oxide. The ortho-arsenite contains 66.0 percent.

When cooled from a temperature of 491°-502°, this substance gave a white condensate of arsenious oxide, followed by an orange-yellow condensate. It therefore appears to undergo thermal dissociation and and the oxidation-reduction simultaneously at this temperature. The temperature was lowered and heating continued for thirteen days at 449°-466° without any apparent change, indicating that neither reaction is reversible at this temperature. The condensates were found to be completely soluble in potassium hydroxide

solution (about 3 N), which indicates that the orange-yellow substance is not elemental arsenic and that it may be the suboxide.

Pure, precipitated ferric oxide was allowed to stand in contact with arsenious oxide solution until the supernatant solution showed a constant titre. It was then filtered and dried at 150°. Titration with iodine gave inconstant results, probably due to the adsorption of arsenious oxide by the ferric oxide precipitated by the bicarbonate. The substance was found to dissolve readily and to give a colorless solution when heated with phosphoric acid. When bicarbonate was added to this, the precipitate formed was almost colorless and therefore did not interfere with the end-point. Titration with iodine under these circumstances gave 44.33, 44.39, and 44.30 percent arsenious oxide. When the substance was heated in air, however, a loss of weight was found which corresponded to the composition of ferric ortho-arsenite, $FeAsO_3$, containing 55.35 percent As_2O_3.

Some of this substance, dried at 150°, was found to give a white condensate when cooled from 300°. When heated to 501°-512°, the condensate was much larger and consisted of vitreous arsenious oxide which cracked the tube on cooling. The fact that no metallic arsenic appeared at the higher temperature suggests that oxidation of the arsenious oxide may have occurred together with reduction of the ferric oxide to magnetite. The residue was found, however, to be quite red and not to be attracted by a small horseshoe magnet. Arsenite could not be detected by the usual test with potassium iodide and hydrochloric acid, because ferric chloride itself sets free iodine. The quantity of arsenious oxide condensed could not be determined because the tube broke.

The results are summarized in Table IV which shows that the reaction

TABLE IV

Initial Reaction Temperatures for the Oxidation-Reduction

Potassium arsenite, 57% As_2O_3	313°-317°
Calcium arsenite, 75% As_2O_3	368°
Zinc ortho-arsenite, 45% As_2O_3	500°-508°
Aluminum arsenite, 50% As_2O_3 (?)	491°-502°

temperature increases with decreasing basicity. None of these figures, except those for zinc ortho-arsenite are to be regarded as accurate, because of the interference of water vapor with the determination. A method has been developed for heating the tubes during evacuation to eliminate the water, and this has been found successful with arsenites which are stable up to 300°.

Determination of Initial Temperatures of Reaction in Evacuated Tubes

A small furnace for heating the tubes during evacuation was constructed like those previously described except that the iron pipe used as the core was smaller, with its internal diameter only a little larger than the external

diameter of the glass tubes used. This furnace was placed in an iron clamp so that it could be tilted at an angle. The current was controlled by means of a lamp-bank, and the temperature was estimated by placing an attached-scale thermometer in the furnace with its stem projecting. The tube containing the sample of arsenite was drawn out so that it could be attached directly to the rubber tube from the vacuum pump, and was constricted very much at one point to facilitate sealing off. The pump was tested by connecting directly to an open-end manometer, and comparing the manometer reading with the barometric pressure. It was found to give a vacuum of less than one millimeter, which was as close as the manometer could be read.

Difficulty was sometimes experienced in finding a temperature at which the water could be driven off without decomposing the arsenite. Substances containing more arsenious oxide than the pyro-arsenite were found to give off arsenious oxide during the evacuation at temperatures lower than the initial temperatures of oxidation-reduction. In the previous experiments attached-scale thermometers were used for temperatures up to 405°. These were checked at the boiling-points of water and naphthalene, and at the freezing-points of potassium dichromate. Two were found that gave 99° at the boiling-point of water, 218° at the boiling-point of naphthalene, and 391° at the freezing-point of potassium dichromate, all measurements taken with about half the scale exposed, as the thermometers were to be used under these conditions. The value for naphthalene was about one degree high and that for dichromate five degrees low, probably due to exposed stem. Since exposed-stem corrections are not applicable to attached-scale thermometers, no corrections were applied. A 570° nitrogen-filled, engraved-scale thermometer was used for higher temperatures and the exposed-stem corrections calculated.

A chromel-alumel thermocouple was also used for temperatures above 400°. This was attached directly to the millivoltmeter without using a cold junction. The room temperature near the furnace was found to be 30°, which corresponds to 1.2 mv. according to the values given in the International Critical Tables, 1, 59. This value was subtracted from the E. M. F. values. The values for the freezing-point of potassium dichromate, lithium chloride, and potassium chloride were then determined and found to check the curve within 2°. The thermocouple was insulated by threading one wire with short sections of small porcelain tubing. It was placed in a Bohemian glass tube which served as a protection tube. The leads were only about one meter in length, so the error due to the resistance of the leads was negligible.

Satisfactory samples of potassium and sodium arsenites could not be obtained by the usual methods, as has been pointed out. An attempt to prepare sodium meta-arsenite by pumping off the necessary amount of arsenious oxide from a sample of the diarsenite at 300°-310° for two hours, resulted in a residue which melted in vacuo at about 400° without darkening and which gave off a small amount of arsenious oxide but no metallic arsenic.

On titrating with iodine it was found to contain 81 percent arsenious oxide, about five percent more than the meta-arsenite.

A substance containing 27.3 percent arsenious oxide prepared from arsenious oxide in ammoniacal solution and lithium chloride, turned brown when heated to about 300°. The residue gave an odor of arsine when placed in cold water, and so the brown color is thought to have been due to the formation of arsenide. Lithium meta-arsenite was sealed off in a Bohemian glass tube after evacuating for one hour at 250°. When heated to 286°-290°, a small condensate of arsenious oxide appeared, and arsenic was observed at 310°-322°. When the tube was heated to 400°, more arsenic appeared but the arsenious oxide did not diminish perceptibly.

A substance containing only slightly more arsenious oxide than barium meta-arsenite was sealed off after evacuation for one hour at about 200°. The substance gave a small condensate of arsenious oxide during evacuation. This was removed from the drawn-off tube after sealing, by dissolving in potassium hydroxide solution. The amount of arsenious oxide seemed to correspond with the excess over that required by the meta-arsenite. When the material in the sealed tube was heated, it darkened at 315°-323°, but no condensate appeared until the temperature was raised to 400°-405°. It seems probable that some arsenic was formed at the lower temperature; but was adsorbed so strongly that it did not appear as vapor. The initial temperature is therefore placed at about 320°. When the tube was heated subsequently at 560°-569°, both arsenious oxide and metallic arsenic condensed, indicating that at higher temperatures both oxidation-reduction and thermal dissociation take place simultaneously. The residue obtained at 579° was almost pure white and gave a very faint odor when placed in cold water, indicating only a very small amount of arsenide.

Calcium meta-arsenate, dried at 140° and sealed in an evacuated tube without further heating, turned brown at 343°-345°, and black when the temperature was raised to 384°-387°. No further change appeared after heating for seven days at 391°-401°. It was thought that water in the sample interfered with the formation of arsenic, but when the tube was evacuated at 200° it lost some arsenious oxide without eliminating all the water, as water condensed when the sample was subsequently heated in vacuo at 308°-311°. It was concluded therefore that metallic arsenic failed to condense because it reacted with the lime to form arsenide, according to the equation

$$As_4 + 3\ CaO = Ca_3As_2 + As_2O_3.$$
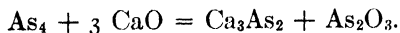
To prove this, the residue was examined and found to give a very faint odor of arsine.

It seemed probable that arsenic is the primary product of the reaction and that the formation of arsenide takes place slowly. To prove this, another sample of calcium meta-arsenite was sealed in an evacuated tube and placed in the furnace at 397°-399° for 24 hours. When removed from the furnace, the substance was found to be yellow. On cooling, it became black and a black condensate appeared in the top of the tube. Thus, by rapid heating

above the initial temperature of reaction, arsenic was produced, whereas it was not produced by raising the temperature slowly, indicating that a secondary reaction took place. However, the possibility is not excluded completely that this is due to water vapor.

A preparation containing 89.8 percent arsenious oxide, with the remainder presumably calcium oxide, was evacuated for one hour and sealed off. A large amount of arsenious oxide was condensed in the constricted portion of the tube. From a titration of this residue was estimated to contain 67 percent arsenious oxide. When this was heated to 313°-321°, it became grayish in color; but no condensate appeared at this temperature or when the sample was heated at 342°-353° for 24 hours. From the weight of the residue it was calculated that the sample must have contained about 62 percent arsenious oxide before undergoing pyrolysis. This is a little less than that required for the pyro-arsenite, $Ca_2As_2O_5$, and indicates that the arsenite is not stable at 250°, and decomposes to form the pyro-arsenite by thermal dissociation; also that the pyro-arsenite, containing a higher proportion of the basic oxide, undergoes oxidation-reduction at a lower temperature than the meta-arsenite. In line with this is the fact that the substance containing less arsenious oxide than the lithium ortho-arsenite, and being therefore a basic arsenite, darkened at a lower temperature. This confirms the view that the basicity of the metallic oxide affects the initial temperature of oxidation-reduction.

A substance containing magnesia and arsenious oxide, approximately in the proportion required to form magnesium ortho-arsenite was dried at 140° and sealed in vacuo without further heating. A condensate of water appeared at 427°-446°, and a white, solid condensate, apparently arsenious oxide, at 469°-473°. No metallic arsenic appeared, even when the temperature was increased to 540°.

Another sample was pumped off for two hours at 285° before sealing. A slight, yellow condensate appeared at 504°-508°, probably a mixture metallic arsenic with arsenious oxide. It was thought that the white color of the condensate in the first instance and the yellow color in the second were both due to incomplete elimination of water. For this reason, another sample was evacuated at 350° for one hour; this gave a very black condensate when cooled from 500°. No water condensed but a drop appeared when the temperature was raised to 531°-537°, and the condensate became brown instead of black.

Zinc ortho-arsenite, dried at 140° and sealed off without further heating, liberated arsenious oxide when heated to 425°-435°, and a black condensate appeared when the temperature was increased to 520°-525°. When the temperature was increased gradually to 590°-595°, the black portion of the condensate disappeared almost completely, leaving the arsenious oxide. This may mean that the reaction is reversed at this temperature or it may mean that arsenide is formed.

Zinc meta-arsenite was dried at 140° and sealed off after evacuating for one hour without further heating. Arsenious oxide just appeared on cooling from 376°-378°. A black condensate first appeared at 496°-508°.

Lead arsenite, containing 41 percent arsenious oxide and corresponding to no definite formula, gave off arsenious oxide when heated to 289°. This disappeared when the temperature was reduced slightly and reappeared when the temperature was raised again. A grayish condensate, apparently metallic arsenic, appeared at 525°-530°. The residue had melted to a yellowish liquid which became white on cooling. Crystals of arsenious oxide also condensed at this temperature.

A substance containing ferric oxide and arsenious oxide in approximately the proportions to form the ortho salt was sealed in an evacuated tube at room temperature. A white condensate appeared when this was cooled from 282°-286°. The amount of this increased with rising temperature; but the heating was continued to 525° without any metallic arsenic appearing.

A product containing approximately 40 percent each of arsenious oxide and alumina, and 20 percent water was evacuated at 370°. The powder appeared to boil at this temperature due to the rate at which adsorbed gases were driven off. The tube was sealed off after having been evacuated for two hours. This substance gave off arsenious oxide at 385°-396°. Water appeared in the tube on cooling from 441°. Heating to 550° produced no further change.

With another sample of the same material evacuation was started at 250° and increased to 450° during two hours. Some arsenious oxide was driven off during the latter part of this evacuation. Water was evidently eliminated by this treatment, as none appeared on cooling the tube. No metallic arsenic was formed even when the tube was heated to 586°.

The results are summarized in Table IV.

TABLE IV

Approximate Formula	Initial Temperature Oxidation-Reduction	Initial Temperature Thermal Dissociation
4 $Li_2O.As_2O_3$	300° approx.	
$Li_2O.As_2O_3$	318°-320°	286°-290°
$BaO.As_2O_3$	315°-323°	Above 500°
$CaO.As_2O_3$	343°-345°	
2 $CaO.As_2O_3$	313°-321°	
3 $MgO.As_2O_3$	500°	
3 $ZnO.As_2O_3$	520°-525°	425°-435°
$ZnO.As_2O_3$	496°-508°	376°-378°
1.3 $PbO.As_2O_3$	525°-530°	289°
$Fe_2O_3.As_2O_3$		282°-286°
$Al_2O_3.50\%As_2O_3$		385°-386°

The general results of this investigation are as follows:—

1.   When a metallic arsenite is heated in an inert atmosphere, there may be thermal dissociation into basic oxide and arsenious oxide; there may be simultaneous oxidation of the arsenious oxide to arsenic oxide and reduction of the arsenious oxide to metallic arsenic which may occur as such or may react further; there may be simultaneous oxidation of arsenious oxide to arsenic pentoxide and reduction of the basic oxide.

2.   If the dissociation pressure of the arsenite is high and the basic oxide is not readily reduced, thermal dissociation may be the only reaction which occurs.   The oxides of aluminium, magnesium, zinc, and lead belong chiefly in this class.

3.   If the dissociation pressure of the arsenious oxide is relatively low and the basic oxide is not readily reducible, the reaction products will be largely arsenic pentoxide and metallic arsenic or a reaction product of arsenic.   The oxides of sodium, potassium, and barium belong chiefly in this class.   For some reason strontium oxide appears to be more nearly like zinc oxide than like calcium oxide.

4.   If the dissociation pressure of the arsenious oxide is relatively low and the basic oxide is readily reducible, the reaction products will be largely arsenic pentoxide and the reduction product of the basic oxide.   The oxides of silver and copper belong chiefly in this class, and ferric oxide to a lesser extent.

5.   There seems almost always to be some thermal dissociation and this is more marked the larger the content of arsenious oxide.   The oxidation-reduction reaction can usually be increased by rapid heating to a high temperature.

6.   When metallic arsenites are heated in the air, oxidation by the air may be superposed on the other reactions.

7.   No experiments have been made at constant pressure and varying volume beyond a few of the evacuation experiments.   It is certain that such a study would give more clear-cut results.

Cornell University.

A STUDY OF GLYCINE ANHYDRIDE

BY IRENE HANNAH SANBORN

Yet another study of glycine anhydride may be of interest—a study undertaken, as it were, in the face of much conflicting evidence, but having as its incentive a theory which is constantly accumulating new supporting facts and correlating many old ones.

Constructive research into the structure of the proteins started with the almost simultaneous pronouncement by F. Hofmeister and E. Fischer of the —CO·NH— linkage as characteristic of proteins. It is not necessary to discuss the well-known peptide theory, or to dwell upon its usefulness. Its relation to the most important criterion in the study of the structure of proteins, namely that furnished by their biological behavior, their reaction with enzymes, is of great import. It is recognized that the breaking down of proteins by chemical means or by peptic and tryptic enzymes has yielded compounds which are of cyclic structure and not straight polypeptide chains. Such cyclic compounds, recognized early in investigations, were 2, 5-dioxopiperazines. These 2, 5-dioxopiperazines are composed of two amino acids, with glycine anhydride in the rôle of their simplest representative.

Although the dioxopiperazines were obtained from proteins comparatively early, no systematic experiments were carried out aiming at their establishment as elementary building stones for the protein structure. The polypeptide theory was too well supported. The possibility, however, of the occurrence of preformed dioxopiperazines was not disregarded by either Fischer[1] or Abderhalden.[2] Fischer states that the simple amide bond does not represent the only possible linkage within the protein molecule, but on the contrary that the occurrence of piperazine rings is rather probable. . . . By intramolecular formation of anhydrides, the numerous hydroxyl groups of hydroxyamino acids can be transformed into ether and ester groups; the variety increasing still more when one considers that the polyamino acids are probable constituents of proteins."

In a comprehensive article by Klarmann,[3] the theories of the cyclic structure of proteins are well discussed and summarized. It is interesting to note that while he considers the pyrrole theory, the dioxopiperazine theory, the experiments of Waldschmidt-Leitz on enzyme separation and subsequent elucidation of protein structure, the synthetic heterocyclic compounds which might possibly occur in proteins, the iso- and allodioxopiperazines, and the ureide theory, he devotes four times as much space to the dioxopiperazine section as to any other. This may or may not be indicative of any particular

[1] Ber., **38**, 607 (1905); **39**, 607 (1906).

[2] "Lehrbuch physiol. Chemie," 3rd ed., 885 (1915).

[3] Chem. Reviews, **4**, 51 (1927).

aptness of this theory. It does mean that the 2, 5-dioxopiperazine structure is one of considerable importance to many who possess an urge to use it in explaining the behavior of proteins.

Not only have homologous dioxopiperazines been repeatedly isolated from the degradation of proteins, but they have also been the object of thorough synthetic work. Curtius and Goebel[4] prepared them from esters of amino acids; whereas E. Fischer by a similar method, studied the transformation of dioxopiperazines into dipeptides. The primary occurrence of the dioxopiperazines was questioned by Abderhalden and Funk[5] and later[6] (1923) confirmed by Abderhalden when he first identified a piperazine derivative obtained from a protein. While in some cases, the anhydrides must be present in a preformed state, in other cases the possibility of a secondary formation cannot be ignored. This has been shown clearly by several workers, among them Grave, Marshall, and Eckweiler,[7] Brigl[8] and finally Abderhalden and Komm.[9,10] The latter have listed[10] the possible tautomeric forms of glycine anhydride as follows:

(A)	(B)	(C)	(D)
O	O	OH	OH
‖	‖	|	|
C	C	C	C
HN CH$_2$	HN CH$_2$	N CH$_2$	HN CH
H$_2$C NH	H$_2$C N	H$_2$C N	HC NH
C	C	C	C
‖	|	|	|
O	O	O	O
	H	H	H
diketo	keto-enol	dienol	diethylene
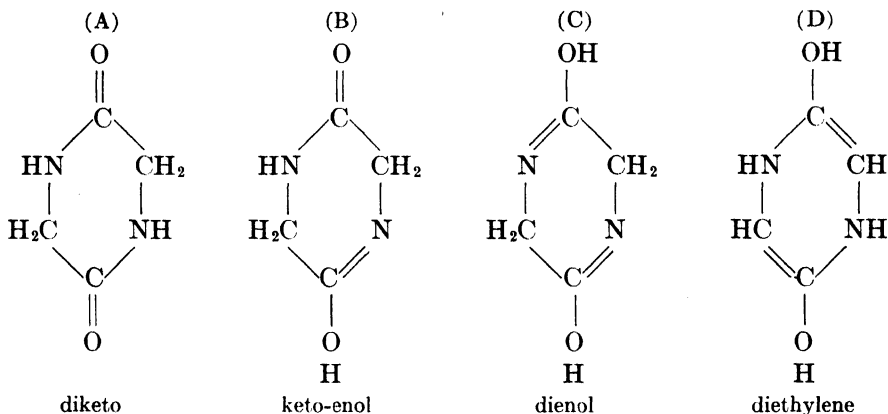
They prepared several derivatives of glycine anhydride and proved their structures—among them, N, N′ diacetyl-2, 5-diketopiperazine; dibenzoyl-2, 5-diketopiperazine; N, N′ dibenzyl-2, 5-diketopiperazine and O,O′ dibenzoylether-2, 5-dioxydihydroxypiperazine. They conclude: "The acceptance of an acid amide linkage for the albumin building stone in the protein molecule is supported by certain facts. Polypeptides, so long as they are built up from the amino acids occurring in nature, are hydrolyzed with few exceptions by ferments which are present in the pancreas and intestinal juice. In case of separation, amino acids are formed by the absorption of water.

One thing is certain, i.e., acid amide-like linked amino acids are present in albumin, and if one assumes that piperazines are also present as building

[4] Ber., **16**, 753 (1883); **17**, 953 (1884).
[5] Z. physiol. Chem., **53**, 19 (1907).
[6] Z. physiol. Chem., **129**, 143 (1923); **132**, 238 (1923).
[7] J. Am. Chem. Soc., **39**, 112 (1917).
[8] Ber., **56**, 1887 (1923).
[9] Z. physiol. Chem., **134**, 121 (1924).
[10] Z. physiol. Chem., **139**, 188 (1924).

stones,—they should be temporary polypeptides—and dipeptides could appear as follows:

OCH₂ CHNH₂ COOH

$$
\begin{array}{c}
\text{OCH}_2\,\text{CHNH}_2\,\text{COOH} \\
| \\
\text{C} \\
\diagdown \\
\text{N} \qquad \text{CH}_2 \\
| \qquad | \\
\text{HC} \qquad \text{N} \\
\text{CH}_3 \diagdown \diagup \\
\text{C OCH}_2\text{CHNH}_2\text{COOH}
\end{array}
\;+\;2\text{H}_2\text{O}\longrightarrow\;
\begin{array}{c}
\text{OH} \\
| \\
\text{C} \\
\diagdown \\
\text{N} \qquad \text{CH}_2 \\
| \qquad | \\
\text{HC} \qquad \text{N} \\
\text{CH}_3 \diagdown \diagup \\
\text{C} \\
| \\
\text{OH}
\end{array}
\;+\;2\;\begin{array}{c}\text{OH}\quad\text{NH}_2\\ |\qquad |\\ \text{CH}_2\cdot\text{CH}\cdot\text{COOH}\end{array}
$$

$$
\begin{array}{c}
\text{OH} \\
| \\
\text{C} \\
\diagdown \\
\text{N} \qquad \text{CH}_2 \\
| \qquad | \\
\text{HC} \qquad \text{N} \\
\text{CH}_3 \diagdown \diagup \\
\text{C} \\
| \\
\text{OH}
\end{array}
\;\longrightarrow\;
\begin{array}{c}
\text{O} \\
\| \\
\text{C} \\
\diagup \diagdown \\
\text{HN} \qquad \text{CH}_2 \\
| \qquad | \\
\text{HC} \qquad \text{NH} \\
\text{CH}_3 \diagdown \diagup \\
\text{C} \\
\| \\
\text{O}
\end{array}
\;+\;\text{H}_2\text{O}\;\rightarrow\;
\begin{array}{c}
\text{O}\\ \|\\ \text{NH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{CH}\cdot\text{COOH}\\ \qquad\quad\ \ \overset{|}{\text{H}}\ \ \overset{|}{\text{CH}_3}
\end{array}
$$
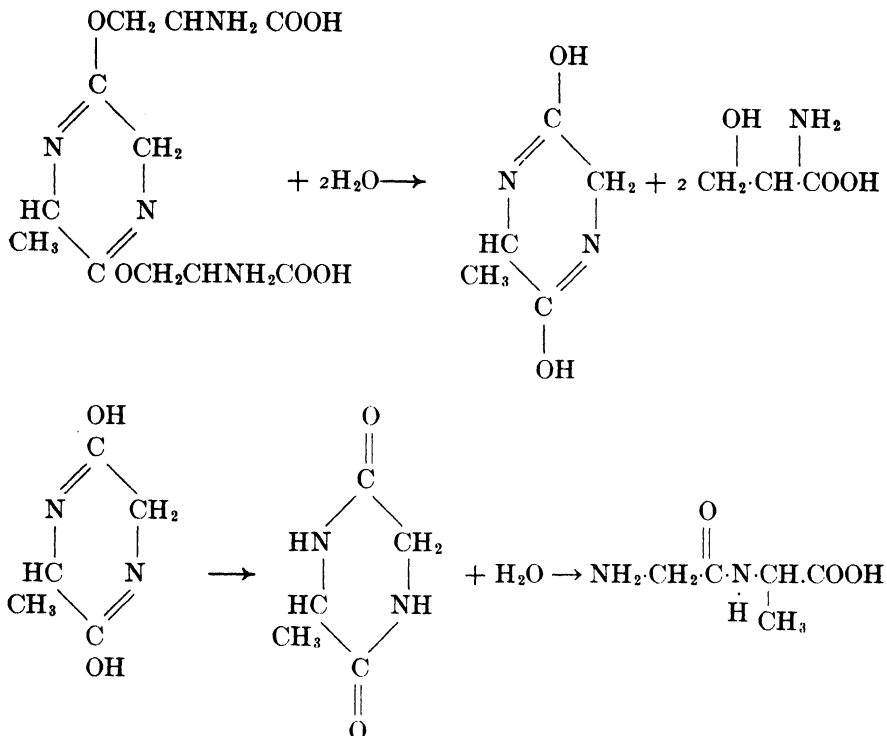
So far it is assumed that a special ferment exists for the building up of the anhydride ring. Every assumption of rings stable toward alkalies and acids, as the piperazine ring, would appear entirely in contradiction with the rapid decomposition of the protein molecule by ferments. It seems then, that the argument of the presence of special ferments would indicate that such ring systems might possibly be in existence. It is not unthinkable that ferments exist which effect the rearrangement, and change one tautomeric form into another whereby in special cases a decomposition of the molecule could be hypothetical.

Any acceptance of a definite structure of the proteins must finally stand in harmony with the facts that the fermentation decomposition as likewise that by acids and alkalies leads to amino acids.

With these requirements the acceptance of anhydrides easily separable by dilute alkalies and dilute acids stands in complete agreement. It is now only the question whether the anhydrides consisting of two amino acids produce 2,5-diketopiperazine, or another form of the same substance.

There is much in favor of the first idea. It is easy to obtain methyl piperazine by reduction from peptized silk. Other piperazines[11] have been isolated

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[11] Z. physiol. Chem., **129**, 143 (1923).

which can originate only from diketopiperazine. There remains the possibility that these are formed secondarily. It is certain that for their origin no dipeptide is to be considered, for among conditions mentioned in the transformation by reduction, no piperazine could be obtained from the polypeptides. Thus, there is probably a tautomeric form. In that case it is possible that the anhydride could occur in relation to amino acids in this form;

$$OCOCHNH_2CH_3$$

$$
\begin{array}{c}
\text{C} \\
\text{N} \quad\quad \text{CH}_2 \\
\text{H}_2\text{C} \quad\quad \text{N} \\
\text{C}
\end{array}
$$

$$OCOCHNH_2CH_2OH$$
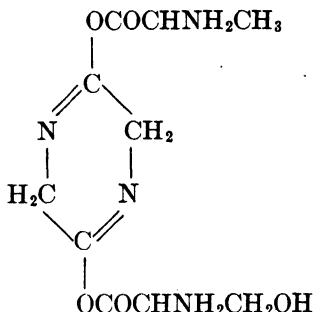
It would actually be possible under these conditions i.e. in the case of reduction, that the amino acids coupled with the anhydride are separated by simultaneous rearrangement of the enol into the keto form. There is much to substantiate the keto structure."

Much evidence exists to show that dioxopiperazines occur in a preformed state, having been extracted from proteins which were cleaved by enzymes or by concentrated acids. Salaskin[12] obtained leucine anhydride by the action of gastric juice on oxyhemoglobin and subsequent extraction with ethyl acetate. Glycyl proline anhydride was isolated from the ether extract of the decomposition product obtained from the action of pancreatin on edestin.[13] These are only two of many similar cases.

Some of the dioxopiperazines appear to be resistant to acid. E. Fischer[14] found that leucine anhydride dissolved in concentrated acids without decomposition, although the ring was split upon prolonged heating. The methods used, aiming at the hydrolysis of the proteins, do not exclude the possibility of a secondary formation of anhydrides; hence mainly interesting from the point of view of dipeptide combinations.

Studies of the reduction and oxidation of proteins contributed more substantial results to the conception of a dioxopiperazine structure. Regardless of how dioxopiperazines might combine with each other, or with amino acids and polypeptides, respectively, it is true that a reduction which prevented the splitting of dioxopiperazines produced volatile piperazines which could be driven off by steam distillation and hence identified. Abderhalden and Stix[15] reduced silk peptone with metallic sodium and amyl alcohol. The distillate gave typical piperazine reactions although the yield was small. This

[12] Z. physiol. Chem., **32**, 592 (1901); **38**, 573 (1903).
[13] Z. physiol. Chem., **47**, 143 (1906).
[14] Ber., **35**, 1164 (1908).
[15] Z. physiol. Chem., **132**, 238 (1925).

did not indicate that the amount of dioxopiperazines in the protein was small, since direct treatment of dioxopiperazine in the same manner also leads to small yields. The dioxopiperazines apparently have low resistances which allow for cleavage in the presence of sodium or sodium alcoholate, whereas only a small portion is reduced. Glycine anhydride and leucyl glycine anhydride were subjected to reduction also and their respective piperazines obtained.[16]

Having contented themselves that the results from reduction pointed toward the probability of the primary occurrence of dioxopiperazine, Abderhalden[17] and his co-workers carried out another series of experiments aiming at the establishment of their presence by oxidation methods. Their results were corroborated by those of Goldschmidt and Steigerwald.[18] All dioxopiperazines yielded oxamide; whereas the dipeptides were decomposed with the exception of glycyl-glycine which also yielded oxamide. With the simplest dioxopiperazine, oxidation takes place thus:

$$
\begin{array}{c}
\text{NH} \\
O\!\!\diagdown\!\!\diagup \quad \diagdown \\
\text{C} \quad\quad \text{CH}_2 \\
| \quad\quad\quad | \\
\text{H}_2\text{C} \quad \text{C} = \text{O} \\
\diagdown \quad \text{N} \diagup \\
\text{H}
\end{array}
\quad + 5\text{O} \longrightarrow
\begin{array}{c}
\text{NH}_2 \\
\diagup \\
\text{C} = \text{O} \\
| \\
\text{C} = \text{O} \\
\diagdown \\
\text{NH}_2
\end{array}
\quad + 2\text{CO}_2 + \text{H}_2\text{O}
$$
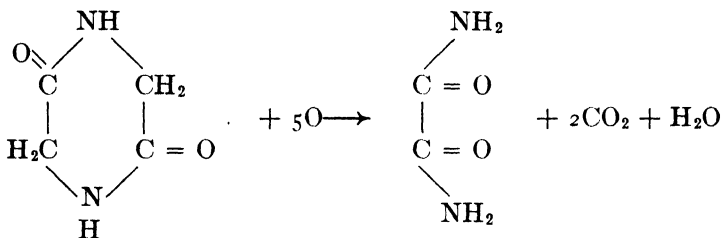
Abderhalden[19] and Komm showed that only polypeptides which contain the glycyl-glycine group would yield oxamide.

$$
\begin{array}{c}
\text{NH}_2 \\
| \\
\text{CH}_2\!\cdot\!\text{CO}\!\cdot\!\text{NH}\!\cdot\!\text{CH}_2\ \text{COOH}
\end{array}
\quad + 5\text{O} \longrightarrow
\begin{array}{c}
\text{NH}_2 \\
\diagup \\
\text{C} = \text{O} \\
| \\
\text{C} = \text{O} \\
\diagdown \\
\text{NH}_2
\end{array}
\quad + 2\text{CO}_2 + 2\text{H}_2\text{O}
$$
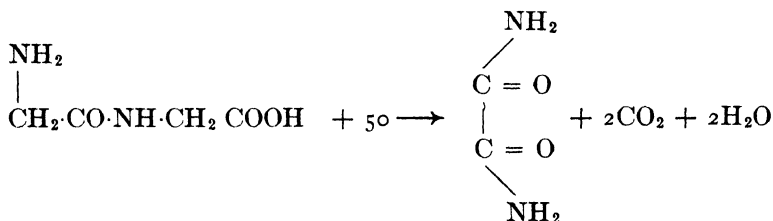
The method was used on the proteins with permanganate as the oxidizing agent. Some proteins were difficultly attacked; but oxamide was obtained from blood globulin, egg albumen, gelatin, caseinogen and silk peptone, thus confirming a well-grounded suspicion.

A comparative investigation of the dioxopiperazines, peptides, amino acids, and proteins or their cleavage products included the application of color reactions which would be specific for one class and would not be given by other classes. Color reactions of the proteins have been long and extensively

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[16] Z. physiol. Chem., **139**, 169 (1924).
[17] Z. physiol. Chem., **140**, 92 (1924).
[18] Ber., **58**, 1346 (1925).
[19] Z. physiol. Chem., **143**, 128 (1925).

useful as means of distinguishing them. Abderhalden and his co-workers[20] after discarding many reagents which showed color with other substances than the dioxopiperazines hit upon a group of reagents, the aromatic nitro compounds, which gave characteristic reactions with dioxopiperazines. Other substances, among them hydantoins, glucose, and malonic ester, gave positive reactions also, but the likelihood of their occurrence in proteins is highly improbable. Picric acid and sodium carbonate will give a positive reaction with all peptones and most of the proteins; whereas, amino acids, and polypeptides do not. m-dinitrobenzene and 3,5-dinitrobenzoic acid give comparable results to those of the picric acid and sodium carbonate. Although these color reactions are not specific, they do constitute another support for the dioxopiperazine theory.

The connection of the dioxopiperazines, which in themselves represent only small complexes, with compounds of high molecular weight, has not been neglected by Abderhalden and his workers. A compound consisting of three molecules of l-proline[21] isolated from a native protein is assigned the tentative formula:

$$
\begin{array}{c}
H_2C\text{----}CH_2 \\
| \qquad | \\
H_2C \qquad CH\cdot COOH \\
\diagdown \diagup \\
CH_2\text{----}CH_2 \\
| \qquad | \\
CH_2 \quad CH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot N \\
\diagdown N \diagup \\
| \\
CO \\
| \\
CH\text{----}CH_2 \\
HN\diagup \qquad | \\
CH_2\text{----}CH_2
\end{array}
$$
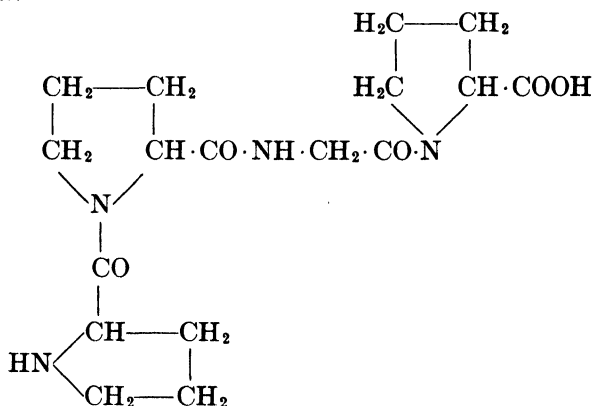
Many compounds of this type could be given as examples[22] to produce an idea as to the assumed nature of combinations of dioxopiperazines and amino acids.

One point, that upon the addition of alkali the amount of $-NH_2-$ nitrogen increases, is of interest as it indicates that the ring is opened on one side by this treatment.

The problem has also been approached synthetically. Abderhalden and Klarmann[23] found that when water is excluded a condensation may take place at a higher temperature with the formation of the corresponding dihalogen acyl-dioxopiperazine.

$$
Cl\cdot CH_2CO\cdot N\diagup\begin{array}{c}CO\text{----}CH_2\\ CH_2\text{----}CO\end{array}\diagdown N\cdot CO\cdot CH_2Cl
$$
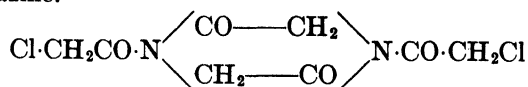
[20] Z. physiol. Chem., 139, 181 (1924); 140, 99 (1924).
[21] Z. physiol. Chem., 127, 281 (1923); 129, 106 (1923).
[22] Z. physiol. Chem., 131, 284 (1923); 139, 169 (1924); 134, 113 (1924); 136; 134 (1924).
[23] Z. physiol. Chem., 135, 199 (1924).

At the same time, Bergmann prepared compounds which probably have the structure $\mathrm{-CH_2}\!\!\diagdown\!\!\diagup\mathrm{N-CO-}$ and are resistant to ammonia.[24]

The structural formula of the dioxopiperazine nucleus allows the assumption of the following tautomeric structures:[25]

$$
\begin{array}{ccc}
\underset{\mathrm{R}}{\mathrm{HN}\diagup\!\!\!\overset{\mathrm{CO-CH}}{\underset{\mathrm{CH-CO}}{}}\!\!\!\diagdown\mathrm{NH}} &
\text{II.} &
\text{III.}
\end{array}
$$
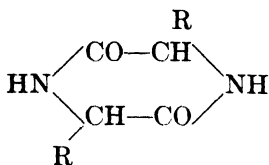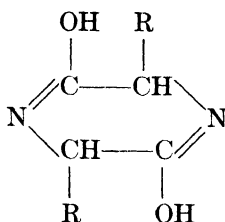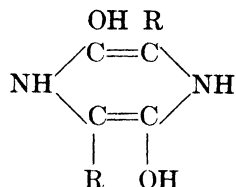
I.   II.   III.

Compounds possessing a markedly unsaturated character were obtained under certain conditions.[26] When glycine anhydride was heated with glycerol in the presence of tyrosine, a compound was isolated which had the empirical composition of glycine anhydride, but in contrast to it immediately decolorized permanganate, gave a positive xanthoprotein reaction and readily allowed the introduction of methyl groups via diazo methane. Abderhalden and Schwab[26] assume that formula III is the most probable for this compound. In the absence of tyrosine the compound obtained loses its unsaturated nature during the course of purification. The rôle of tyrosine is not quite clear. Rearrangement of the enol form of 2,5-dioxopiperazine into its keto form took place by heating in aqueous solution to 90-100°.[27]

Dioxopiperazines were obtained in the enol form by heating the respective dipeptides with diphenylamine.[28] Several enolic anhydrides, among them, d,l-leucyl-glycine, d,l-leucyl-d,l-valine, were prepared in excellent yields. Glycyl-glycine and glycylalanine behaved differently from the other dipeptides. The first gave a difficultly soluble compound, probably a polymer, with composition of glycine anhydride. The dioxopiperazines in the keto form are not changed into the enol form by heating with glycerol or diphenylamine, but the change is effected by heating with aniline. A proof for the assumed structure (I) is given by preparing the anhydride from alpha-amino-isobutyryl-alpha-aminoisobutyric acid. The anhydride cannot exist in the enol form on account of its particular structure.

[24] Z. physiol. Chem., **140**, 128 (1924); **143**, 108 (1925); **146**, 247 (1925); **152**, 189 (1926).
[25] Z. physiol. Chem., **139**, 64 (1924); Naturwissenschaften, **13**, 99 (1925).
[26] Z. physiol. Chem., **149**, 100 (1925).
[27] Z. physiol. Chem,. **152**, 90 (1926).
[28] Z. physiol. Chem., **152**, 125 (1926).

```
   OH  R·                          CH₃   CH₃
    |   |                             \   /
    C═══C                           OC────C
   /     \                          /      \
  HN      NH                       HN       NH
   \     /                          \      /
    C═══C                            C────CO
    |   |                          CH₃⁄  \CH₃
    R   OH
     I.                              II.
```
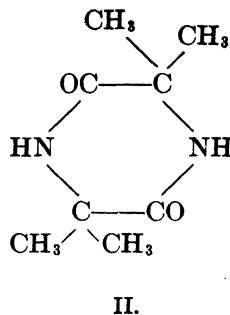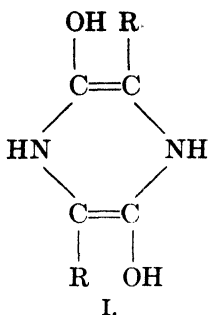
The product gave all anhydride reactions, but unlike other anhydrides prepared by the same method, did not give the xanthoprotein reaction or decolorize permanganate. Since it was possible to obtain sarcosine anhydride in the unsaturated form,[29] the existence of the —C = C— linkage in enolic dioxopiperazines seems close to establishment.

Methods have been devised to distinguish between these tautomer compounds in a physical way. Abderhalden and Haas have found that several amino acid anhydrides give a characteristic absorption in the ultraviolet, the enol form showing a more pronounced absorption than the keto form. Some proteins also absorb in the ultraviolet. The absorption spectrum of an amino acid depends on the method of its preparation. In one case, the enol-keto rearrangement could be observed spectroscopically in d, l-leucyl-glycine anhydride. The rearrangement was complete after eight hours.[30] Abderhalden continued this particular bit of his work by examinations via polarized light of the copper salts of optically active amino acids and their polypeptides.[31] Moreover his conclusion based upon this and further studies of absorption in the ultraviolet region by polypeptides,[32] is that when treated with alkali, amino acids assume an inner anhydride structure; whereas, in the case of polypeptides where the inner anhydride structure is improbable, no absorption is shown. Such studies were continued[33] and the absorption spectra for several aromatic amino acids and their derivatives were determined, among them, 3,5-diiodotyrosine anhydride.

Shibata[34] and Asahima in their investigations of desmotropy of dioxopiperazines prepared glycine anhydride, alanine anhydride, and sarcosine anhydride by heating the corresponding amino acids in glycerol according to Balbiano[35] and Maillard.[36] None of the compounds showed an absorption spectrum; hence the conclusion that they existed in the keto form only. There would appear to be a disagreement between these observations and those of Abderhalden and Haas.

Other interesting observations, capable of utilization for structural investigations of the dioxopiperazines are: 1) the refractive index of the enol

[29] Z. physiol. Chem., **153**, 83 (1926).
[30] Z. physiol. Chem., **155**, 202 (1926).
[31] Z. physiol. Chem., **164**, 37 (1927).
[32] Z. physiol. Chem., **164**, 1 (1927).
[33] Z. physiol. Chem., **166**, 78 (1927).

form is found to be higher than the keto form;[34] 2) the optical rotation of solutions of dioxopiperazines decreases under the influence of x-rays and ultraviolet rays, while that of the corresponding peptides remains unchanged. The formation of ozone under irradiation may cause oxidation.

Abderhalden[37] and Schwab have evidence that the cleavage of enolic dioxopiperazines leads to unsaturated peptides. Glycyl-glycine prepared from enolic glycine anhydride behaves differently from that obtained from the keto form in that it decolorizes permanganate, gives the xanthoprotein reaction, no anhydride reaction, and dissolves in aqueous sodium hydroxide, giving solutions bright yellow in color. The color disappears upon heating. d,l-leucyl-glycine shows a similar behavior. The two forms of leucyl-glycine behave differently toward alkalies, the saturated form being unchanged while the unsaturated form is split quantitatively.

Anhydride rings such as glycyl-d-alanine, which may undergo cleavage due to action of alkali, are undoubtedly of use in enzymic digestion. Glycine-l-tyrosine anhydride, on the other hand, is rendered more susceptible to alkali cleavage by the action of enzymes. Abderhalden and Schnitzler[38] studied this by the formation of copper salts. Open chain structures with a —COOH group form copper salts immediately; otherwise the anhydride ring must be broken by an alkali before salt formation can occur. The change was detected by changes in rotation using a quartz-mercury lamp.

In the further preparation of diketopiperazines, an unsaturated anhydride from d-l-leucyl glycine anhydride is mentioned[39] although no comments are made concerning its structure. It is resistant to hydrolysis by normal alkalies, adds bromine, gives an intense red picric acid reaction, shows strong absorption in the ultraviolet, and hydrolyzes with dilute sulphuric acid to yield glycine, ammonia, and alpha-keto caproic acid. Another paper[40] indicated other combinations of diketopiperazine with amino acids, i.e. leucyl glycine anhydride with glycine anhydride gives a crystalline substance.

A still later report of Abderhalden and Mahn[41] concerning the action of alkali, acid, and enzymes on proteins, polypeptides and 2,5-diketopiperazines decides that acids and alkalies act in the same manner though at different velocities, their action alone furnishing no insight into the behavior of the diketopiperazine groupings which are probably present in these proteinoids.

According to Karrer,[42] the double bonds are not in the position assumed by Abderhalden and Schwab. Karrer states that the dibenzyl compound is derived from an enolic form for which he suggests the following formula:

[34] Bull. Chem. Soc. Japan, 1, 71 (1926).
[35] Ber., 33, 2323 (1900); 34, 1501 (1901).
[36] Compt. rend., 153, 1078 (1911); Ann. Chim., (9) 1, 519, 2210 (1914).
[37] Z. physiol. Chem., 154, 99 (1926).
[38] Z. physiol. Chem., 164, 159 (1927).
[39] Z. physiol. Chem., 163, 149 (1927).
[40] Z. physiol. Chem., 164, 274 (1927).
[41] Z. physiol. Chem., 174, 47 (1928).
[42] Helv. Chim. Acta, 6, 1108 (1923).

$$\text{O·CH}_2\text{·C}_6\text{H}_5$$

$$\text{O·CH}_2\text{·C}_6\text{H}_5$$
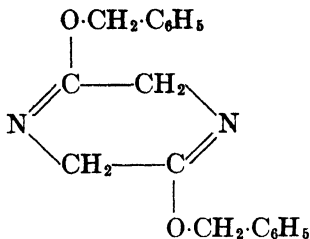
The enolic form, moreover, must possess a higher reactivity, since it was previously found that glycine anhydride must be heated with chloroacetyl chloride in the presence of nitrobenzene to 160° in order to effect substitution; and the dichloroacetyl compound results on heating the dibenzyl dioxopiperazine with chloroacetyl chloride on a water bath.

Maillard[43] in his study of compounds formed from glycine anhydride (2,5 diketopiperazine) states that 2,5 diketopiperazine does not possess a sufficiently basic character to form with acids, salts stable in the presence of water or alcohol. Fischer and Fourneau[44] have shown the same thing to be true. They showed that the "chlorhydrate of glycine anhydride" obtained by Th. Curtius and Fr. Goebel[45] by boiling the anhydride with concentrated hydrochloric acid and recrystallizing from alcohol is none other than the chlorhydrate of glycyl-glycine: $HCl·NH_2·CH_2·CO-NH·CH_2,COOH$. The action of the hot acid has broken down the ring structure of the piperazine. Maillard confirmed this work by repetition. Moreover, being interested in an investigation of crystalline compounds which would permit preparation and differentiation by microscopic observation, he sought to differentiate between the chloroplatinates of cyclo glycyl-glycine, glycyl-glycine, tri glycyl-glycine and glycine anhydride. All his efforts furnished exactly the same substance quite regardless of whether his initial reactant was cyclo glycyl-glycine or glycyl-glycine,—analysis indicating the following formula—$(HCl·NH_2·CH_2·CO·NH·CH_2·COOH)_2$ Pt $Cl_4·2H_2O$. This substance is evidently identical with that described by Th. Curtius and Fr. Goebel to which they attributed the formula $(NH·CH_2·CO)_4(HCl)_2·PtCl_4 + 3H_2O$.

When Maillard tried to prepare the chloroplatinate of 2,5-diketopiperazine, he states that the piperazine ring is opened at once as in the case of the chlorhydrate.

Another sidetrack was investigated by Zelinski and Gavrilov[46] in their work on the anhydride nature of the proteins. They find the proportion of glycine anhydride to vary in proteins, being highest in gelatin and lowest in sturine. Their method is to carry out acid hydrolysis by autoclaving dipeptides and anhydrides. Hydrolysis of aqueous solutions of dipeptides results in the formation of anhydrides which increases with the concentration of the dipeptide solution. Since the synthesis of anhydrides is inhibited by weak

[43] Ann. Chim., (9) 1, 542 (1914).
[44] Ber., 34, 2868 (1901).
[45] J. prakt. Chem., (N.F.) 37, 178 (1888).
[46] Biochem. Z., 182, 11 (1927).

acid and suppressed by 1 molar acid, their formation in autoclave hydrolysis appears impossible.

Goldschmidt and co-workers[47] report that upon treating diketopiperazines with hypobromic acid, no decomposition occurs in neutral solution, but only a normal bromination of the ring. Morel and Preceptis[48] find that picric acid hydrolyzes 2,5-diketopiperazine to glycyl-glycine; while Levene and co-workers[49] find the rate of hydrolysis of diketopiperazine much lower when a methyl group is substituted on the α carbon.

Yaichnikov[50] reports the hydrolysis of 2,5-diketopiperazines and dipeptides as monomolecular reactions, and Olander[51] finds the basic dissociation constant of diketopiperazines in 0.01 N NaOH too small to be measured electrometrically, and the acid dissociation constant to be 7×10^{-14}. Stiasny and Scotti,[52] in their study of the acid-alkali binding power of peptides, have run a series of titration curves to determine whether the peptide unions play a part in the acid and alkali binding power of peptides. They used glycine, and its mono, di, and tri homologues in order to have an increasing number of peptide unions along with one —NH₂ and one —COOH group. At the same time they ran glycine anhydride. Their results showed glycine to behave like a weak monacidic base and a weak monobasic acid. The addition of hydrochloric acid at first greatly diminished the pH value of its solution and then slowly decreased the pH value of the resulting buffer. After the addition of one equivalent of hydrochloric acid, the curve coincided with that of hydrochloric acid itself. The curve for glycine anhydride indicated that there was no acid binding and only a very slight binding of the alkali.

Another interesting sidelight upon the structure of the enol form of diketopiperazine is found in some work of Richardson, Welch, and Calvert.[53] They found that diketopiperazine did not condense with aromatic aldehydes upon fusion. The Perkin reaction (sodium acetate and acetic anhydride) seemed to be the only method to prepare derivatives of diketopiperazine without acetylation of amino nitrogen. Even so the reaction was not general; aliphatic aldehydes did not form simple 3,6 derivatives, and though generally applicable to the aromatic series, O-hydroxy-subaldehyde gives poor yields. By this reaction condensations of vanillin, cinnamaldehyde, piperonal, salicylaldehyde, tolualdehyde and O-chlorobenzaldehyde with glycine anhydride were effected. Diketopiperazine failed to condense with benzylidene aniline on fusion. Likewise, all attempts to condense diketopiperazine with substituted amidines have been unsuccessful. There would appear to be five possible enol forms:

[47] Ann., **456**, 1 (1927), Proteins IV.
[48] Compt. rend., **187**, 236 (1928).
[49] J. Biol. Chem., **81**, 697 (1929).
[50] Biochem. Z., **190**, 114 (1927).
[51] Z. physiol. Chem., **134**, 381 (1928).
[52] Ber., **63B**, 2977 (1930).
[53] J. Am. Chem. Soc., **51**, 3074 (1929).

$$
\begin{array}{ccccc}
\text{H} & & \text{H} & \text{H} & \\
\text{N} & \text{N} & \text{N} & \text{N} & \text{N} \\
\text{HC}\quad\text{COH} & \text{H}_2\text{C}\quad\text{COH} & \text{H}_2\text{C}\quad\text{COH} & \text{H}_2\text{C}\quad\text{COH} & \text{H}_2\text{C}\quad\text{COH} \\
\text{HOC}\quad\text{CH} & \text{HOC}\quad\text{CH}_2 & \text{HOC}\quad\text{CH} & \text{O}=\text{C}\quad\text{CH} & \text{O}=\text{C}\quad\text{CH}_2 \\
\text{N} & \text{N} & \text{N} & \text{N} & \text{N} \\
\text{H} & & & \text{H} & \text{H} \\
\text{I.} & \text{II.} & \text{III.} & \text{IV.} & \text{V.}
\end{array}
$$

enol forms   half enol forms
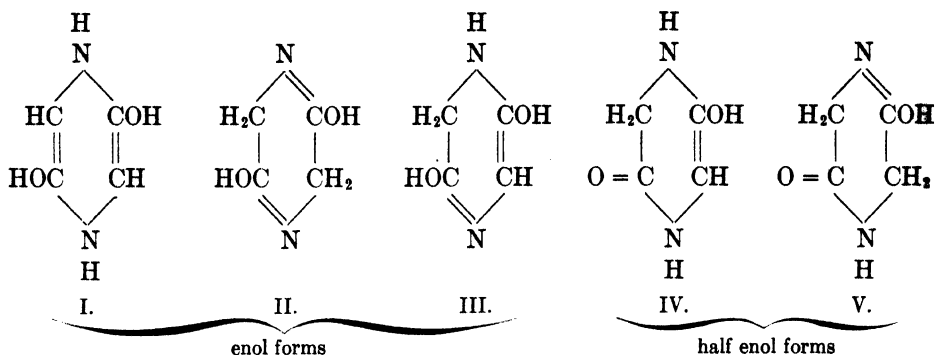
The proof of the presence of hydroxyl groups in the enol form of diketopiperazine is based mainly upon color tests, i.e. positive xanthoproteic and a negative picric acid reaction. Definite confirmation of their presence is that two moles of α naphthyl isocyanate condense easily with one mole of diketopiperazine. Probably there is only one enol form present in appreciable quantity. Concerning the structure of that one we know that there are two hydroxy groups by its behaviour with isocyanate. In order to determine the predominant enol form, a condensation with m-nitrobenzaldehyde was tried.

If compound   I—no condensation, therefore no —CH$_2$— groups.

If compound II—condensation, with two aldehyde groups.

If compound III—condensation with one aldehyde group.

Upon condensation, the product showed a nitrogen content of 14.73%, an amount identical with that obtained from condensation of glycine anhydride and m-nitro benzaldehyde. If enol form (II) had resulted, the condensation product would have 11.70% nitrogen, and if enol form (III), 13.21% nitrogen.

The probable explanation seems to be that during the course of the reaction the isocyanate first hydrolyzed, forming enol-diketopiperazine, which reverted to a more stable keto form and then condensed with the aldehyde. One would expect (II) to condense without hydrolysis, but (I) must hydrolyze before condensing. Analysis showed that nearly complete hydrolysis has taken place, therefore (I) must be the ordinary form of diketopiperazine.

To confirm this, another condensation was made with tolualdehyde. The resulting compound has a nitrogen content of 8.81%, while the condensation product of the diketopiperazine derivative of α naphthyl isocyanate has 8.92%. Hence, the probability of —C = C— is supported, since α naphthyl isocyanate derivative condenses with aldehydes only after hydrolysis.

If one is justified in making deductions based upon researches into the polysaccharides, it can be assumed that associations of elementary complexes are present in the proteins. Although only a working hypothesis, the conception has seemed so convincing that the existence of specifically acting disaggregating enzymes was assumed by Oppenheimer.[54] Pepsin was relegated to the rôle of a non-hydrolyzing ferment whose disaggregating mechan-

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[54] "Die Fermente und ihre Wirkungen," 2, 811, 1208 (1926).

ism was to dissolve the subordinate valences which held together the elementary complexes. Delightful though this theory might be, it could not be corroborated by experiment.

Certain experiments have been adduced in favor of the existence of associated compounds. Pfeiffer and Wittka[55] showed that certain dioxopiperazines, among them glycine anhydride, are capable of forming molecular combinations with various salts, amino acids and organic compounds. The following are described as well-crystallized compounds:

$$CaCl_2, NH \underset{\diagdown CO\ -CH_2 \diagup}{\overset{\diagup CH_2-CO \diagdown}{<}} NH,\ 2H_2O$$

$$2LiCl, NH \underset{\diagdown CO\ -CH_2 \diagup}{\overset{\diagup CH_2-CO \diagdown}{<}} NH,\ 2\tfrac{1}{2}\ H_2O$$

$$2LiBr, NH \underset{\diagdown CO\ -CH_2 \diagup}{\overset{\diagup CH_2-CO \diagdown}{<}} NH,\ 2\tfrac{1}{2}\ H_2O$$
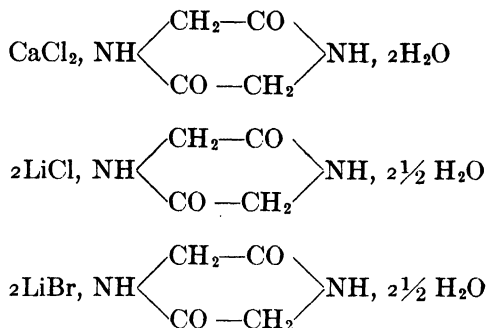
Sarcosine compounds with sodium iodide, potassium bromide, potassium iodide and rubidium bromide were easily obtained, whereas Pfeiffer and Angern[56] found sarcosine anhydride to give molecular compounds with tryptophane, scatole, anthranilic and p-aminobenzoic acids.

Asahina and Tsurumatsu[57] have prepared other molecular compounds with heavy metals. By mixing hot solutions of glycine anhydride with salts of heavy metals, and evaporating to incipient crystallization, the following compounds were obtained in crystalline form: $C_4H_6N_2O_2 \cdot 2HgCl_2$, $C_4H_6N_2O_2$ $UO_2Cl_2 \cdot H_2O$, $C_4H_6N_2O_2\ UO_2(NO_3)_2$, $C_4H_6N_2O_2\ CdCl_2$. All of these are insoluble in organic solvents, but soluble in water with separation into their components. There are probably many formulations of these compounds, the metal in each case being linked directly with the nitrogen. There might be a possibility of breaking the double bond in case of the $-C = N-$ linkage, and this linkage might be ruled out since the compounds are soluble in water and later separate. In the case of the $-C = C-$ enol form, there could be simple addition to the nitrogen, which is what one might expect.

The anhydride linkage is referred to again by Speakman and Hirst[58] who claim that in the breaking down of the keratins, the anhydride linkage is broken before the disulphide bond is attacked.

Considering the abundance of interest, evidence, and work which the anhydride linkage excites, any contribution which may further elucidate the structure of its simplest building stone, glycine anhydride, should be of some value.

[55] Ber., **48**, 1292, 1306 (1915).
[56] Z. physiol. Chem., **143**, 265 (1925).
[57] Z. physiol. Chem., **186**, 133 (1929).
[58] Nature, **127**, 665 (1931).

A résumé of this work finds much evidence in favor of the diethylene formula for the enol form of glycine anhydride. All of Abderhalden's work, whether that of synthesis or analysis, oxidation or reduction or a study of absorption spectra indicates a preference for the —C = C— configuration. The contributions of Goldschmidt, Richardson, Welch and Calvert are also in agreement. Shibata and Asahina apparently continue to prefer the diketo formula only.

Another point of agreement appears to be that glycine anhydride is incapable of reacting with acids without subsequent hydrolysis to form either glycine or glycyl glycine. The work of Maillard, Moreland and Levene is evidence, quite regardless of the titration curves submitted by Stiasny and Scotti.

Goldschmidt finds, however, that in neutral solution, glycine anhydride is brominated at points of unsaturation by hypobromic acid without decomposition, and Fischer finds the ring structure resistant to concentrated acids unless prolonged heating is used.

The work of Bancroft and Barnett in studying the behavior of protein and protein-like substances with ammonia and hydrogen chloride has done much to show the true nature of these weakly basic and weakly acidic substances. Because glycine anhydride presents a molecule containing two nitrogen atoms in conjunction with either two carbonyl groups for the diketo form or two
$$\overset{\text{H}}{}$$
ethylene groups, or just possibly the —N = C— configuration, for the enol forms, it seemed desirable to check its behavior with hydrogen chloride. The slightly basic character of the nitrogens would be quite covered if they existed in either the diketo or diethylene configuration in accordance with the deductions made by Bancroft and Barnett. If, however, glycine anhydride showed any inclination to form even an adsorption complex, there would still be the possibility for it to react with a more active acid which might make the most of these very weakly basic tendencies and so form compounds.

With this in mind, glycine anhydride has been studied in relation to hydrogen chloride, perchloric acid, sulphuric acid, and hydrofluoric acid. With the exception of hydrogen chloride, compounds have been prepared in each case. With hydrogen chloride, glycine anhydride forms an adsorption complex—although C. L. A. Schmidt of the University of California[59] may be able to construe even these data to show the formation of a real compound.

The behavior of glycine anhydride with hydrogen chloride was studied by means of a mechanism similar to the one used first by Bancroft and Barnett in their work on Phase Rule Studies on the Proteins.[60]

The apparatus used for these determinations is a modified form of the original, and is described in careful detail by B. C. Belden in his work on Gelatin with Ammonia and Hydrogen Chloride.[61] See Fig. 1. The discussion in that paper[61] regarding the behavior of samples at high and low gas pressures,

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[59] J. Biol. Chem., **87**, 327-335 (1930).

[60] J. Phys. Chem., **34**, 449-498, 753-798, 1217-1253, 1930-1946, 2433-2471 (1930).

[61] J. Phys. Chem., **35**, 2172 (1931).

impossibility of obtaining equilibrium points quickly, the tendency of apparatus to leakage, are very much to the point in this study with glycine anhydride as well as with gelatin.

Working at a fairly constant temperature (22°-24°C.), varying measured quantities of dry hydrogen chloride are added to a dry weighed sample of glycine anhydride. The apparatus having been carefully calibrated, the amount of gas in the apparatus is readily calculated from an observation of the pressure levels of the manometer. As the glycine anhydride combines with the dry hydrogen chloride the manometer levels change until such a

FIG. I
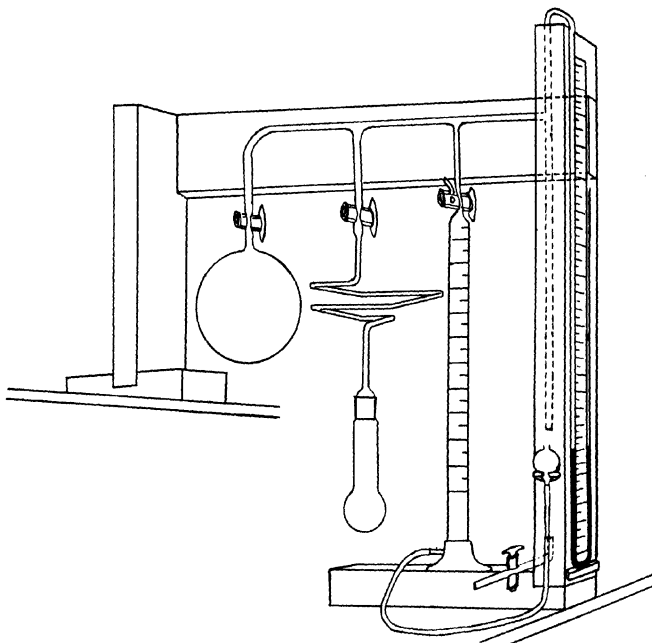
time as an equilibrium point may have been reached. A further addition of dry hydrogen chloride will lead to the establishment of new equilibrium points. The theory of this apparatus operates upon Gibb's Phase Rule, $F+P=C+2$. We have two components, glycine anhydride and hydrogen chloride. If a compound is formed, we shall have three phases, namely, glycine anhydride, glycine anhydride hydrochloride and hydrogen chloride. We have used up our one degree of freedom, the temperature variable, and hence our system is defined. If, however, we are dealing with an adsorption complex, there will be only two phases and the system will have two variables, allowing a change of pressure with concentration of hydrogen chloride while the temperature remains constant.

The glycine anhydride used in the determination is a product of the Eastman Kodak Company. No effort was made to check the purity of the product

as similar studies have shown that the presence of moderate amounts of water or other impurities tend to displace curves, although the type of curve obtained is not altered.[62]

The samples used were dried by standing in a desiccator over concentrated sulphuric acid and anhydrous sodium carbonate for at least a week.   Sample 4
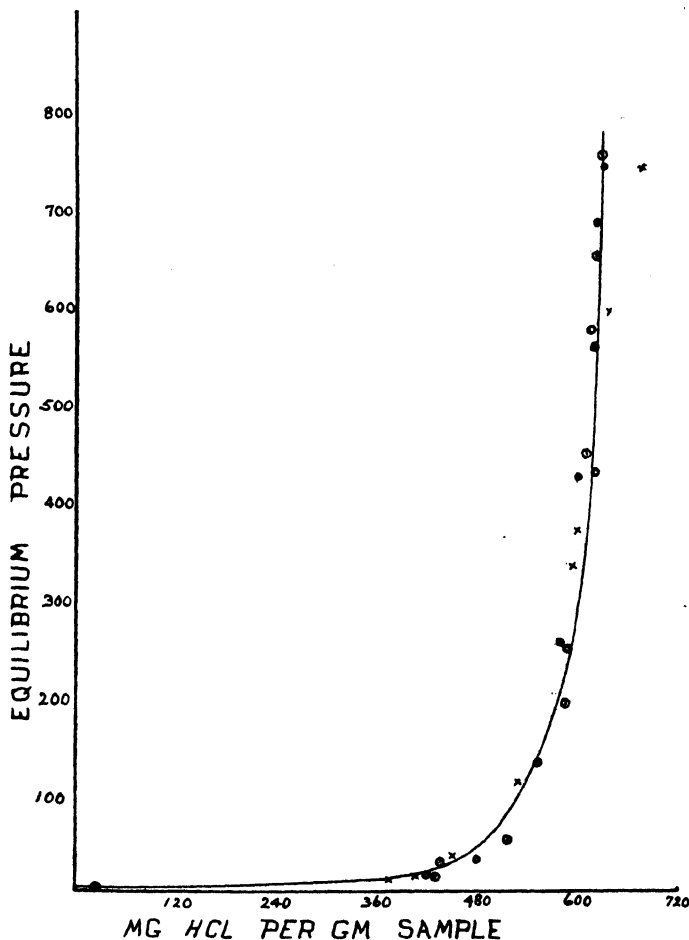
Fig. 2

Glycine Anhydride and Hydrogen Chloride

Sample 1 ●   Sample 3 ○
Sample 2 ✕   Sample 4 ⊙

remained over concentrated sulphuric acid for several months before it was run.   It will be noted that the points for this sample are in accord with the other data.

Glycine anhydride, like some other compounds (gelatin and tribromaniline) appears to reach its equilibrium points more quickly when it is under a considerable gas pressure.   Points determined from the up-curve of a substance

[62] J. Phys. Chem., **34**, 491 (1930).

having a high initial adsorption, hence a low gas pressure, are likely to mean little. Months would be required to reach the true equilibrium points by this method. For this reason, a large volume of dry hydrogen chloride was added in each case, and then given volumes withdrawn, allowing the system to reach a new equilibrium point after each withdrawal

At a pressure of 750 mm. dry hydrogen chloride was taken up at a rate of 6 mm. per minute. The reaction flask was shaken, keeping the finely divided solid in motion and preventing any caking. In another case where the reaction flask was agitated only occasionally, the time required to reach an equilibrium point was four hours, with a change in manometer level amounting to 69 mm. or 0.29 mm. per minute. In general, equilibrium points were reached at high gas pressures within 10-15 minutes when the sample was agitated. Each equilibrium point was read only after the manometer had remained constant for several hours.

The data for four typical samples are found in Tables I, II, III, and IV, while the curve obtained by plotting equilibrium points against milligrams hydrogen chloride per gram sample are found to form a curve which can be recognized easily as that of an adsorption isotherm. See Fig. 2. The curve is smooth at junction with lowest pressures. There is, moreover, no reason to expect compound formation at this point. If glycine anhydride, molecular weight 114, combined with two moles of hydrogen chloride the ratio (73:114)

TABLE I

(1) Sample 0.604 gm. Dry

Volume HCl added cc.	Volume HCl removed cc.	Net vol. cc.	P_2 mm.	Volume remaining up cc.	Volume taken up cc.	Wt. HCl taken up mgm.	Wt. HCl taken up per gm. sample mgm.
546		546	736	312	234	384	636
	29	517	679	288	229	376	622
	177	400	420	178	222	364	603
	80	320	253	107	213	349	578

TABLE II

(2) Sample 0.508 gms. Dry

Volume HCl added cc.	Volume HCl removed cc.	Net vol. cc.	P_2 mm.	Volume remaining up cc.	Volume taken up cc.	Wt. HCl taken up mgm.	Wt. HCl taken up per gm. sample mgm.
336		336	366	149	187	307	603
179		515	736	302	213	349	687
	76	439	588	240	199	327	642
	119	320	330	135	185	304	597
	108	212	110	47	165	271	532
	53	159	36	14	145	238	467
	22	137	15	7	130	208	408
	16	121	11	4	117	192	378

would be 640 mg. hydrogen chloride per gram glycine anhydride, or if for some reason only one of the nitrogens of glycine anhydride were active and a compound consisting of one mole glycine anhydride to one mole hydrogen chloride were formed, the ratio 36.5:114 would give 320 mg. hydrogen chloride per gram glycine anhydride. Inspection of the curve of Fig. 2 shows that nothing of the sort is indicated.

TABLE III

(3) Sample 0.574 gms. Dry

458							
		458	570	243	215	355	618
	60	398	434	180	218	357	623
	88	310	245	105	205	336	587
	56	254	130	57	197	323	564
	70	184	36	16	168	276	481
	30	154	16	7	147	241	421

TABLE IV

(4) Sample 0.915 gms. Dry

675							
		675	749	323	352	577	631
	50	625	645	277	348	571	624
	44	581	553	235	346	567	620
	49	532	445	190	342	561	613
	126	406	190	80	326	535	585
	92	314	52	20	294	482	527
	48	266	33	19	247	405	443
	15	251	12	6	245	402	438
	237	14	3.5	1.7	12.3	20.2	22

The diketo formula for glycine anhydride is not in keeping with its behavior with hydrogen chloride. The presence of any methylene groups surely would tend toward activating the glycine anhydride sufficiently to cause compound formation even though the methylene groups are adjacent to the carbonyl. Richardson's[53] enol forms (2) and (3) do not seem applicable, since they possess

(2)   (3)
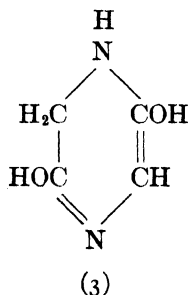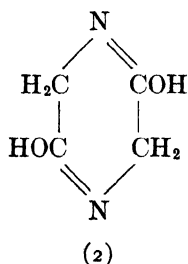
active methylene groups.   Richardson's enol form (1)

$$
\begin{array}{c}
\text{H} \\
\text{N} \\
\diagup \quad \diagdown \\
\text{HC} \qquad \text{COH} \\
\| \qquad \| \\
\text{HOC} \qquad \text{CH} \\
\diagdown \quad \diagup \\
\text{N} \\
\text{H}
\end{array}
$$
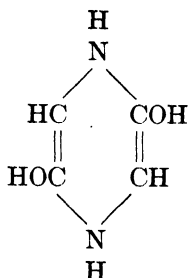
however, contains no active methylene groups and the activity of the imino nitrogens is reduced by the adjacent ethylene linkages, thus giving a possible explanation for the formation of an adsorption complex rather than a true compound.

The basis for such reasoning, it may be recalled, appears in certain of the phase rule conclusions[60], namely that:

(1)   Carbonyl groups attached directly to the nitrogen, or an aliphatic ethylene carbon linkage decrease the tendency of the nitrogen to react stoichiometrically with hydrogen chloride. (2) Two keto linkages or one keto and one ethylene linkage will destroy the tendency to add hydrogen chloride unless compensated by the presence of alkyl groups.

In the diketo form (p. 1803) each nitrogen is attached on the other side to a methylene group and the diketo form would therefore add two hydrogen chlorides.   In enol forms (2) and (3) we have not even the partial effect of the keto group and the enol forms would also add two hydrogen chlorides.   In Richardson's half enol form (IV) p. 1810, it is possible that the presence of one active methylene group would sufficiently activate the imino nitrogen so that the molecule could combine with one hydrogen chloride.   His enol form (1) however, containing two ethylene linkages, and no carbonyl groups could not possibly combine with hydrogen chloride to form a compound.   The existence of an adsorption complex is however in keeping with our theory.

Glycine Anhydride Hydrofluoride

The behavior of glycine anhydride with hydrogen chloride having been determined, interest was felt concerning any reaction with hydrofluoric acid. Anhydrous hydrofluoric acid is very soluble in water.   At its boiling point, 19.4°C. it has a vapor density H_4F_4 although at 90° it is practically HF. In water solution there is no evidence of any molecule containing more than two fluorine atoms.   According to Sidgwick,[63] the highest polymer must contain F-H←F-H with 2-covalent fluorine, but this is evidently unstable.   In water, hydrofluoric acid occurs as the single or double molecules HF and H_2F_2 or their ions.   It has been shown that while the polymerized form is a strong acid $H(F_2H)$ and is wholly ionized, the true dissociation constant of the simple HF is only 7×10^{-4},

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[63] "The Electronic Theory of Valency," 270 (1927).

so that the weakness of hydrofluoric acid as compared with the other halogen acids is only partly explained by its polymerization. Sidgwick concludes, "whereas other halogen hydrides are practically completely ionized in H_2O, H_2F_2 is mainly covalent. This is a particularly surprising fact in view of the greater tendency of fluorine to ionization, which is established both practically and theoretically." In the hydrogen compound this is overcome by the unusual strength of its covalent link to hydrogen. The same theory accounts for the peculiar tendency of the fluoride ion to hydrate, i.e. F ion being negative, attaches itself to hydrogen of the water. Moreover, while fluorine itself has an unusually low covalency, it tends to bring out the highest covalences of other atoms with which it combines, i.e. $(F_2H)^{--}$, AsF_5, IF_5, SF_6, SeF_6 and OsF_8. The other halogens offer no analogues. The cause may very well be the small size of the fluorine atom, whereas other halogens readily assume covalency of more than one with greater ease as atomic number increases. Hence the very

$$\text{stable} \quad \begin{array}{c} \text{H-O} \qquad \text{O} \\ \diagdown \qquad \nearrow \\ \text{Cl} \\ \diagup \qquad \diagdown \\ \text{O} \qquad \quad \text{O} \end{array} \quad \text{, perchloric acid.}$$
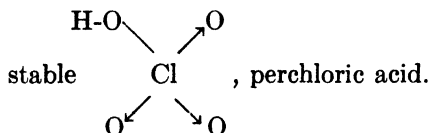
Preparation of Hydrofluorides

The methods of preparation used can conveniently be classified as follows:

A.   Organic Method: Use of 48% hydrofluoric acid solution:

Crystalline glycine anhydride treated with 48% hydrofluoric acid solution (Sterling Chemicals or Baker's Analyzed) until just dissolved, then added in excess, placed in ice bath and the hydrofluoride precipitated with ether; filtered and dried between filter papers.

B.   Reaction in Solution: Use of 48% hydrofluoric acid solution:

Crystalline glycine anhydride was treated with excess 48% hydrofluoric acid solution in paraffin-coated evaporators, placed in paraffined vacuum desiccators over stick sodium hydroxide and exhausted to 9 mm. The uncombined hydrofluoric acid was removed during the evacuation, leaving a dry solid in the evaporator. The amount of hydrofluoric acid which combines with glycine anhydride depends upon the length of time which the acid solution and glycine anhydride were in contact before drying in the desiccator.

C.   Use of liquid hydrofluoric acid:

Since the boiling point of liquid anhydrous hydrofluoric acid (H_4F_4) is 19.4°C., it should be possible to prepare it as such from a salt working at a sufficiently low temperature; and thence by raising the temperature to bring the gaseous hydrogen fluoride (HF or H_2F_2) into direct contact with the basic substances in whose reaction we have interest.

With this in mind crystalline c.p. potassium acid fluoride was placed in a large platinum dish containing small platinum crucibles. The depths of the crucibles was considerably less than the depth of the platinum dish. The samples of finely divided bases, i.e. glycine anhydride, guanidine carbonate, etc., were placed in the crucibles, and the large platinum dish was surrounded by an ice-concentrated hydrogen chloride freezing mixture at − 15°C. A

volume of concentrated sulphuric acid was brought to the same temperature, and gradually added to the KHF₂ surrounding the crucibles. At the low temperature the reaction proceeded slowly with a layer of a thin colorless liquid forming over the surface of the KHF_2. The dish was held at a temperature below 0°C. until a sufficient volume of cold concentrated sulphuric acid had been added to form twice the amount of hydrogen fluoride necessary to form the maximum compound possible between the base and the acid. The dish was then sealed by Pregl's wax with a large watch glass whose surface was protected by a thick coating of the same wax. The temperature of the bath surrounding the platinum dish was gradually raised through successive baths of cracked ice, and cold H_2O, until it had reached room temperature. Evidence of the progress of the reaction was had by noting the escape of hydrogen fluoride through a small vent made in the wax of the seal. From time to time the platinum dish was opened, some of the contents of the crucibles removed, the platinum dish recharged with KHF_2 and the experiment repeated. In this manner it was possible to judge when the maximum hydrofluoride possible with this method had been formed. Quantitative calculations of amounts of KHF_2 and concentrated c.p. sulphuric acid were made on the basis of the following reaction:

$$KHF_2 + H_2SO_4 = H_2F_2 + KHSO_4$$
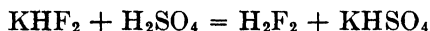
Upon removing samples from the reaction vessel, they were placed over stick sodium hydroxide in paraffined vacuum desiccators. In the case of each sample note the times during which the sample was held in the reaction chamber, and kept in either evacuated or unevacuated desiccator.

Note: Theoretically it should be possible to use paraffined glassware for this preparation, but because of the tendency of paraffin to crack at low temperatures and to melt at temperatures above 35°C., platinum dishes were used.

Method of Analysis

Samples were weighed into small weighed pyrex beakers, dissolved or suspended in distilled water, and the hydrofluoric acid set free subsequent to hydrolysis, was titrated immediately with standard sodium hydroxide in the presence of phenolphthalein.

This method corresponds for the most part to the conventional volumetric method advocated by Treadwell and Hall.[64] They use platinum dishes coated with beeswax, add an excess of standard sodium hydroxide and titrate the excess of the latter with an acid of known strength.

Six samples from the same preparation of glycine anhydride hydrofluoride were treated in pairs as follows: a) exactly according to Treadwell and Hall method; b) using paraffined beakers and titrating directly with standard sodium hydroxide; c) using uncoated pyrex glass beakers and titrating directly with standard sodium hydroxide.

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[64] "Analytical Chemistry," Vol. II, 7th Ed., p. 498.

The analyses in all three cases checked. Since the third method of procedure is a ready one and the phenolphthalein end-point is best recognized in glass, it has been used throughout the analyses. The Treadwell-Hall method is undoubtedly very desirable for samples containing a high concentration of hydrofluoric acid, and it does do away with the necessity of immediate titration; whereas the reasons for the success of the simpler method are undoubtedly: first, the fact that the hydrofluoric acid set free is titrated before it has a chance to attack the glass, and secondly, that the samples used are small and hence set free correspondingly small amounts of the hydrofluoric acid. The two factors are easily taken care of by titrating the samples immediately after weighing them.

Phenolphthalein appears to be a suitable indicator for the titration not only from the point of view of pH, but also because of the tendency of hydrofluoric acid to form acid salts by adding onto neutral salts normally set free in titration. This is another example of the tendency of hydrofluoric acid to bring out the maximum covalency of the substances with which it is in contact, i.e. $NaF \cdot HF$ and $BaF \cdot 2HF$. Characteristic reactions according to Winteler:[65]

$$2HF + NaOH \rightarrow NaF \cdot HF + H_2O$$

$$NaF \cdot HF + NaOH \rightarrow 2NaF + H_2O$$
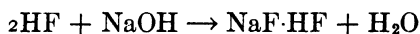
The data presented in Tables V, VI, and VII and in Fig. 3 indicate something more than the formation of an adsorption complex between the glycine anhydride and hydrofluoric acid. The combination with mole portions of hydrofluoric acid rather than some fractional part can not be mere chance. The maximum compound formed by any method used successfully appears to be one corresponding to what one might have predicted from Sidgwick's discussion of hydrofluoric acid, namely that although fluorine itself has a particularly low covalency it tends to bring out the highest covalencies of the atoms with which it combines.

Data for:

Method A—Organic method using 48% hydrofluoric acid solution.

<center>TABLE V</center>

Samples	(1)	(2)
	0.2384	0.1568
cc. NaOH 0.2033 N required for titration	7.94	5.16
equivalence in grams of HF	0.0323	0.0210
% HF in sample	13.5%	13.4%
Mole equivalent to H	0.91	0.90

[65] Z. angew. Chem., 1902, 33.
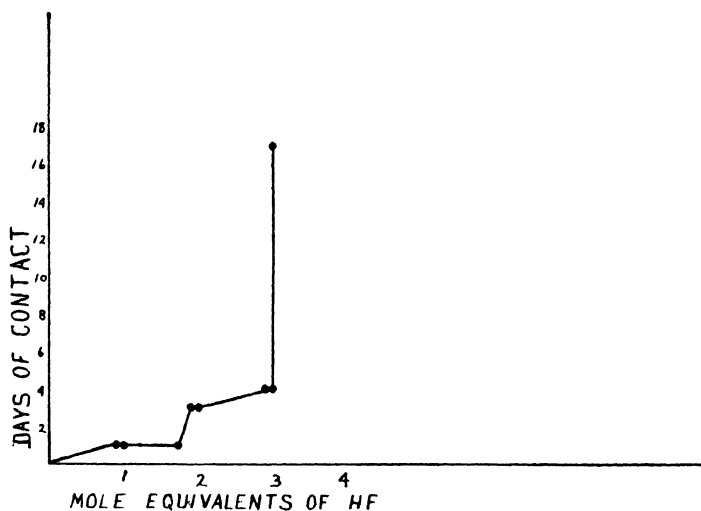
FIG. 3

Glycine Anhydride and Hydrofluoric Acid

TABLE VI

Data for: Method B—Use of 48% hydrofluoric acid solution.

History of samples:

Sample	(1)(2)(3)	(4)(5)	(6)(7)	(8)(9)
Contact time	1 day	3 days	4 days	17 days
Drying time	1 day	1 day	1 day	2 days

Appearance: dry white solid.

Samples		cc. NaOH 0.1562 N needed for titration	Equivalence in grams of HF	% HF in sample	Mole equivalent to HF
	gm.	cc.	gm.	%	
(1)	0.2802	13.48	0.0421	15.0	1.01
(2)	0.2740	22.44	0.0702	25.6	1.97
(3)	0.3458	14.84	0.0464	13.4	0.90
(4)	0.1806	11.65*	0.0473	26.2	2.00
(5)	0.0776	4.76*	0.0194	25.0	1.92
(6)	0.3120	34.51	0.1180	34.5	3.00
(7)	0.2753	29.22	0.0916	33.2	2.88
(8)	0.1666	14.32*	0.0583	35.0	3.00
(9)	0.2233	18.77*	0.0765	34.2	2.97

* Used NaOH 0.2033N for titration
1 mole equivalent of HF = 14.9%
2 mole equivalent of HF = 26.0%
3 mole equivalent of HF = 34.5%
4 mole equivalent of HF = 41.2%

These data expressed graphically (see Fig. 3) indicate that the maximum combination with HF by this method is in the molecular ratio of 1:3.
Data for: Method C—Use of liquid anhydrous hydrofluoric acid.

<div align="center">TABLE VII</div>

History: 4 days in reaction chamber.

        Samples (1) and (2) held in unevacuated desiccator 2 days.

        Samples (3) and (4) held in desiccator evacuated to 4 mm. 2 days.

Appearance: while, dry, friable, with strong odor of HF.

Samples	(1)	(2)	(3)	(4)
	0.0997 g.	0.0781 g.	0.1423 g.	0.1422 g.
cc. NaOH 0.1206 N. needed for titration	17.03	12.33	22.99	21.88
Equivalence in grams of HF	0.0411	0.0298	0.0555	0.0530
% HF in sample	41.2	38.2	39.0	40.7

Average percentage of HF in samples: 39.8%
Mole equivalent in HF: 3.86.

These data correspond to the theoretical possibility of a compound between one mole of glycine anhydride and four moles of HF or two moles of H_2F_2, that is, to a maximum combination in the ratio of 114:80 or 41.3%. Furthermore, there appears to be little tendency for the hydrofluoride to decompose under reduced pressure conditions.

The behavior of glycine anhydride with hydrofluoric acid, reacting in simple molecular ratios, indicates that the anhydride must possess a somewhat more basic nature than the work of Stiasny and Scotti[66] would favor.

A consideration of the work done by Hofmann and his co-workers with perchloric acid, in which he obtained well-defined crystalline perchlorates, caused the present experimenter to hope for the formation of a perchlorate of glycine anhydride. In his extensive work, Hofmann[67] has prepared and analyzed, among others, such crystalline compounds as the perchlorates of fluorescein, diazo toluidin, diazonium aniline, pyridine, carbazol, phenanthrene and triphenyl amine. He[68] states in translated form: "Perchloric acid is

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[66] Ber., 63B, 2977 (1930).

[67] Ber., 39 (3), 3146 (1906); 59 B, 448 (1926); 43 (1), 178, 183 (1910); 42 (2) 2031, 4856 (1909).

[68] Ber., 43 1080 (1910).

a convenient means of studying the basic characteristics of carbon and oxygen substances. Like no other acid, perchloric is able to turn to account the smallest amount of affinity of the chief and secondary valences for the formation of beautiful crystalline compounds. It surpasses in this respect, as we shall show by the examples of triphenylamine and tritolyamine, even picric acid, and is suitable, in most cases even better than that, for the separation of carbinols, ketones and amines from resinous admixtures. In general it is sufficient to treat the solutions in ether, benzene, tetrachlorethane, or carbon tetrachloride with seventy percent perchloric acid in order to obtain completely pure perchlorates. If the above-named liquids will not serve as solvents, one can use the concentrated acid itself as a solvent and filter off the crystals through clay, in which case resinous impurities stay in solution; or one can evaporate the acid in vacuum over phosphorus pentoxide or calcium oxide at ordinary temperatures. One obtains particularly beautiful crystals from an acetic acid solution mixed with perchloric acid when one concentrates this in a vacuum. Against the wide-spread opinion to the contrary, perchloric acid acts at room temperature, even up to 100°C., non-oxidizingly, and the handling of seventy percent perchloric acid is scarcely dangerous."

According to the data obtained with hydrofluoric acid, it should be possible for glycine anhydride to combine with perchloric acid in the ratio of 1:2; thus providing additional evidence for the existence of an enol form. If, however, the ratio proved to be 1:1 something might be said for the existence of glycine anhydride in one of Richardson's[69] half enol forms.

The perchloric acid used for the preparation was approximately 71.5% perchloric acid prepared from the concentrated commercial perchloric acid according to Hofmann's[70] directions by evaporating to 140°, and then distilling. Most of the distillate came over at 200°C, the boiling point of the dihydrate, and this solution, consisting of a mixture of the mono and dihydrate, approximately 71.5% perchloric acid, was used for the reaction.

Since glycine anhydride is insoluble in alcohol, acetic acid, chloroform and carbon tetrachloride as well as other common organic solvents, it was eventually treated in one of two ways; either Method A, by suspending it in absolute alcohol, adding the perchloric acid until solution had occurred, and placing in vacuum desiccator over P_2O_5 until a crystalline mass separated; or Method B, adding the acid directly to the crystalline glycine anhydride in sufficient excess to bring about solution, concentrating somewhat on hot plate; and finally placing in vacuum P_2O_5 desiccator until crystallization has occurred. Either procedure appeared to be successful and analyses from crystals prepared by each method tallied.

Small quantities of reagents were used, usually not more than one gram of glycine anhydride with always an excess of perchloric acid. Three or four

[69] J. Am. Chem. Soc., 51, 3074 (1929).

[70] Ber., 42, 4856 (1909).

days in the frequently evacuated desiccator passed before the separated crystals were filtered through sintered glass and dried on clay in a P_2O_5 desiccator.

Samples were weighed and titrated directly with standard sodium hydroxide using phenolphthalein as an indicator. Titration provides a sharp end-point.

It has been a matter of considerable interest to compare the method of procedure used in this work with that of Read and Campbell[71] in an analysis of similar compounds; for instance, diphenyl ethyl amine derivatives such as sulphonates and cyanides. In these cases the authors titrated first to an end-point with standard aqueous sodium hydroxide and then added alcohol or some inert organic solvent in which the salt liberated was soluble, and again titrated to an end-point. The alcohol acting as a solvent for the salt, thus removed any acidity or basicity due to its hydrolysis by decreasing or preventing its dissociation.

This procedure seems totally unnecessary and even somewhat in error if a proper selection of indicator has been made in the first place. Let us suppose for instance, that one is titrating the salt of a weak base and strong acid with sodium hydroxide. An indicator should be selected which will show an end-point somewhere in the 8-10 pH range; in other words, one which is sensitive to a slight excess of base. This end-point will represent the stoichiometrical end-point of the titration. If alcohol is added, assuming our salt to be soluble in it, the salt is removed, the effect of its hydrolysis is no longer felt and the titrated mixture again becomes colorless. More sodium hydroxide must be added to compensate for the removal of the weakly basic salt. This too, is an end-point, at pH 7, the point of true neutralization, but it is not the end-point representing the stoichiometrical relationship in which we are interested.

A microscopic examination of the crystals prepared by each method showed them to be colorless hexagonal prisms, optically anisotropic, with side views of prisms exhibiting parallel extinction. No confusion of these crystals with the fine needles of glycine anhydride would be likely.

The perchlorate melted sharply at $117°$ at 742 mm. on the Dennis-Shelton melting-point block.

One factor causing some difficulty in an otherwise simple procedure was that the perchlorate of glycine anhydride is an extremely deliquescent substance. First analyses made on samples weighed and titrated at the usual laboratory rate showed varying results; moreover, samples dried only a few days would show a difference in percentage of combined perchloric acid amounting to 7-8%, compared to samples taken from the same preparation and dried for a longer period.

The following data represent two series of analyses made on the same preparations from samples which were dried for different intervals.

[71] J. Chem. Soc., 1930, 2377, 2674.

Glycine Anhydride Perchlorate

TABLE VIII

Series I

Days dried before analyzing	13	14	15
Sample	0.2912 g.	0.1314 g.	0.1151 g.
cc. NaOH 0.1012 N required for titration	14.40	7.09	6.53
Equivalence g. HClO$_4$	0.1465	0.0721	0.0664
% HClO$_4$	50.3	55.0	57.7

Preparation was exhausted at this stage.

TABLE IX

Series II

Days dried before analyzing	13	26	27	28
Sample	0.1396	0.2336	0.2400	0.2398
cc. NaOH 0.1012 N required for titration	7.32	14.59	14.89	14.88
Equivalence g. HClO$_4$	0.0745	0.1483	0.1515	0.1515
% HClO$_4$	53.4	63.5	63.2	63.2

By a wiser disposition of the preparation analyzed in Series II the maximum time for drying was settled. It is possible that a month may be a longer time than is necessary for an equilibrium to be reached. No work was done to check that point.

The analyses for four typical samples of the perchlorate of glycine anhydride follows (Table X).

TABLE X

Method of Preparation	A	A	B	B
Drying time (days)	28	28	28	28
Sample	0.2429	0.2367	0.2435	0.2432
cc. NaOH 0.1012N needed for titration	15.10	14.78	15.23	15.29
Equivalence g. HClO$_4$	0.1539	0.1503	0.1550	0.1555
% HClO$_4$	63.4	63.5	63.7	63.8

A consideration of the possibilities of perchlorates which could be formed from glycine anhydride included the following:

				%HClO^9
(a) diperchlorate of glycine anhydride—Mol.Wt.		315	63.8
(b) monoperchlorate '' '' — '' ''		214.5	46.8
(c) glycine perchlorate '' '' — '' ''		175.5	57.3
(d) glycyl glycine perchlorate '' — '' ''		232.5	43.2

The data obtained indicate only one of these, namely the diperchlorate of glycine anhydride.

If one were considering only the perchlorate data, either the diketo or diethylene formula for glycine anhydride would be suitable. Its behavior with hydrogen chloride rules out the keto formula because of the presence of the active methylene groups. The greater activity of perchloric acid, however, would easily account for compound formation with the imino nitrogen of the diethylene formula whereas hydrogen chloride might not be active enough. Such would appear to be the case. The behavior of glycine anhydride with concentrated sulphuric acid and hydrofluoric acid would also appear to be in harmony with the choice of the diethylene formula as the usual enol form.

The procedure used with concentrated sulphuric acid follows:

Glycine anhydride was treated with a large excess of concentrated sulphuric acid in a glass beaker. There was no evidence either of reaction or of solution. The mixture was poured onto a watch glass in a vacuum desiccator over phosphorus pentoxide and evacuated to 11 mm. On the following day, the soft white residue was transferred from the watch glass to a piece of porous plate and returned to the vacuum desiccator over phosphorous pentoxide. Its appearance on the following day was that of a white brittle substance, readily powdered. Upon standing, it combined greedily with moisture in the atmosphere.

Analysis: Samples were weighed rapidly and titrated with standard sodium hydroxide in the presence of phenolphthalein as an indicator.

The data for four typical samples follow representing two different preparations:

TABLE XI

Weight of sample (g.)	(1) 0.5741	(2) 0.5070
cc. NaOH 0.102 N required for titration	72.88	63.89
Equivalent gms. NaOH	0.2954	0.2585
Equivalent gms. H_2SO_4	0.3620	0.3170
% H_2SO_4 in sample	63.25	62.50

TABLE XII

Weight of sample (g.)	(3) 0.1476	(4) 0.1568
cc. NaOH 0.2033 N required for titration	9.40	10.08
Equivalent gms. NaOH	0.0765	0.0807
Equivalent gms. H_2SO_4	0.0935	0.0988
% H_2SO_4 in sample	63.35	63.10

If one mole of glycine anhydride combines with one mole of sulphuric acid the molecular ratio would be 114:98, or a compound with 46.2% sulphuric acid; whereas if one postulates a one to two ratio, that is, 114:196, the percentage of sulphuric acid would be 63.25%. The data obtained from the analysis indicate the formation of a disulphate.

All results obtained serve as additional evidence for the diethylene enol form, a form already in excellent repute. The compounds reported in this paper are in accord with Sidgwick's theory of covalency. Nitrogen has a maximum covalency of four with its fifth, an electrovalence. In the case of combination with perchloric acid, $\quad$ O $\quad$, Sidgwick's

$$H - O - Cl \rightarrow O$$

with the structure showing O above (↑) and O below (↓) the Cl.
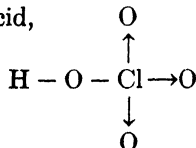
formula, the imino nitrogens of glycine anhydride must share their two unused electrons with the hydrogen of perchloric acid. The configuration of glycine anhydride diperchlorate or better, the perchloric acid derivative of 2,5-dihydroxy diethylene piperazine is probably this:

$$
\left[\begin{array}{c} O \\ \uparrow \\ O \leftarrow Cl - O \\ \downarrow \\ O \end{array}\right]^{-}
\begin{array}{c} H^{+}:NH \\ \diagup \diagdown \\ HC \qquad COH \\ \| \qquad \| \\ HOC \qquad CH \\ \diagdown \diagup \\ HN:H^{+} \end{array}
\left[\begin{array}{c} O \\ \uparrow \\ O - Cl \rightarrow O \\ \downarrow \\ O \end{array}\right]^{-}
$$
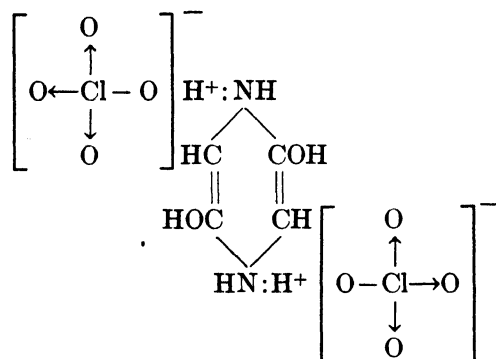
Since the maximum amount of hydrofluoric acid combining with one mole of glycine anhydride is four moles, and since there are only two nitrogens in each molecule of glycine anhydride, hydrofluoric acid must be existing in its polymerized form H_2F_2. This form, mainly covalent, is represented by the formula $F - H \leftarrow F - H \leftarrow$. Its highest compound with glycine anhydride

will be: $^{-}[F - H \leftarrow F] H^{+}:NH$

$$
\begin{array}{c} \diagup \diagdown \\ HC \qquad COH \\ \| \qquad \| \\ HOC \qquad CH \\ \diagdown \diagup \\ _{H}N:H^{+} [F \rightarrow H - F]^{-} \end{array}
$$
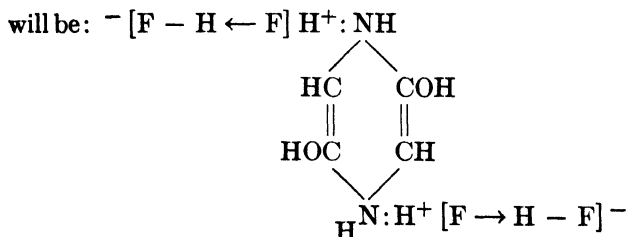
whereas the lesser combinations would be represented by:

$$
^{-}[F] H^{+}:NH \qquad\qquad ^{-}[F] H^{+}:NH \qquad\qquad NH
$$

$$
\begin{array}{ccc}
\begin{array}{c} \diagup \diagdown \\ HC \quad COH \\ \| \quad \| \\ HOC \quad CH \\ \diagdown \diagup \\ _{H}N:H^{+}[F \rightarrow H - F]^{-} \end{array}
&
\begin{array}{c} \diagup \diagdown \\ HC \quad COH \\ \| \quad \| \\ HOC \quad CH \\ \diagdown \diagup \\ _{H}N:H^{+}[F]^{-} \end{array}
&
\begin{array}{c} \diagup \diagdown \\ HC \quad COH \\ \| \quad \| \\ HOC \quad CH \\ \diagdown \diagup \\ _{H}N:H^{+}[F]^{-} \end{array}
\end{array}
$$
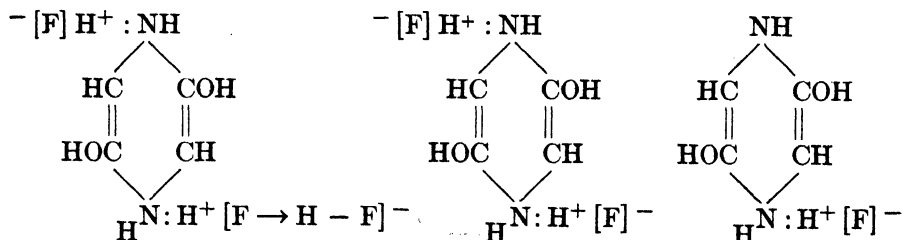
The sulphuric acid derivative could be written in a similar manner, i.e.:

$$\left[\begin{array}{c} O \\ \uparrow \\ O \leftarrow S - O \\ | \\ OH \end{array}\right]^{-} \begin{array}{c} H^{+} : NH \\ \diagup \diagdown \\ HC \quad\ COH \\ \| \quad\quad \| \\ HOC \quad\ CH \\ \diagdown \diagup \\ HN : H^{+} \end{array} \left[\begin{array}{c} O \\ \uparrow \\ O - S \rightarrow O \\ | \\ OH \end{array}\right]^{-}$$
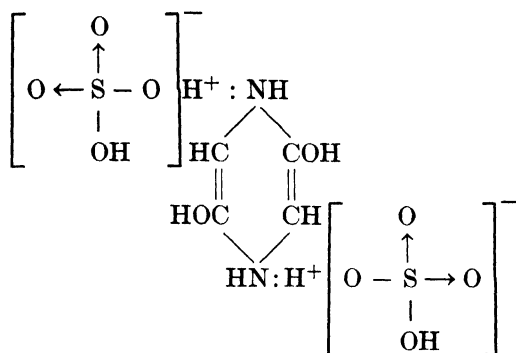
An application of the Phase Rule to the systems discussed in the preparation of the hydrofluoric acid, perchloric acid and sulphuric acid derivatives of glycine anhydride finds all except one to be three-component systems. In the preparation of the hydrofluoride by the use of liquid anhydrous hydrofluoric acid, Method C, we have a two-component system, namely glycine anhydride and hydrofluoric acid, or glycine anhydride hydrofluoride and glycine anhydride, or glycine anhydride hydrofluoride and hydrofluoric acid, existing in two phases, gas and solid. The Phase Rule[72] $F = C + 2 - P$, reading in this case, $F = 2 + 2 - 2$, or $F = 2$, limits the system to two degrees of freedom, a divariant system where the concentration is constant and the temperature may be varied.

In each of the other cases, the addition of an acid solution to glycine anhydride with the subsequent separation of the glycine anhydride derivative from solution, the systems are three component ones, existing in two phases having three variables, temperature, pressure, and concentration.

Summary

The principal points made in this paper are:

1. It would appear from this work that glycine anhydride has a somewhat greater acid-binding power than has been considered probable.

2. Glycine anhydride forms an adsorption complex with hydrogen chloride.

3. Glycine anhydride forms a series of compounds with hydrofluoric acid, the molecular ratio of combination depending upon time of contact and concentration of acid. The maximum compound is that formed by the combination of two moles of polymerized hydrofluoric acid (H_2F_2) with one mole of glycine anhydride.

4. With perchloric acid, a more active acid than hydrogen chloride, a crystalline perchlorate is formed having a composition which indicates the combination of one mole of glycine anhydride with two moles of perchloric acid.

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[72] Findlay: "The Phase Rule and Its Applications."

5.   Similarly with sulphuric acid, glycine anhydride is found to form a disulphate.

6.   The compounds and adsorption complex studied in this paper present more evidence for the diethylene configuration of the enol form of glycine anhydride.

7.   The possibility of preparing crystalline compounds with perchloric acid and very weakly basic nitrogen compounds has been indicated.   More data concerning the formation of other crystalline perchlorates will appear in an early paper.

8.   The ability of hydrofluoric acid to bring out the maximum covalency of the imino nitrogen of glycine anhydride has been used as a hypothesis for the formation of other hydrofluorides.   An early report will supply more information.

9.   The method of titrating a strong acid set free by the hydrolysis of a salt in the presence of a weakly basic substance using phenolphthalein as an indicator has been utilized throughout the analyses of the perchlorates, hydrofluorides and sulphates.

10.   It is probable that the behavior of glycine anhydride may explain in

$$\text{H} \qquad \text{O}$$

part the behavior of zein which probably contains no $- \overset{..}{\text{N}} - \overset{..}{\text{C}} -$ linkages.

Throughout this paper the name glycine anhydride has been conscientiously used.   The experimenter preferred to show no structural preference, until sufficient experimental data had been collected to justify a choice.   The evidence submitted here is construed in favor of 2,5-dihydroxy diethylene piperazine.:

$$
\begin{array}{ccc}
 & \text{H} & \\
 & \text{N} & \\
 & \diagup\diagdown & \\
\text{HC} & & \text{COH} \\
\| & & \| \\
\text{HOC} & & \text{CH} \\
 & \diagdown\diagup & \\
 & \text{N} & \\
 & \text{H} &
\end{array}
$$
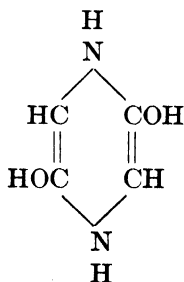
Cornell University.

AN ANALYSIS OF THE ADSORPTION PHENOMENA WITH SILICA GEL AT LOW TEMPERATURES

BY WM. D. URRY[1]

(A). The Mercury Diffusion Pump as a Gas Collector

In dealing with very small quantities of gas it is often required to pump these gases from an apparatus of large volume and quantitatively collect them again at atmospheric pressure. Such a process has been described by Peters and Weil.[2] · In principle the apparatus here described is similar. The introduction of an automatically operated "Toepler" and burette, however,
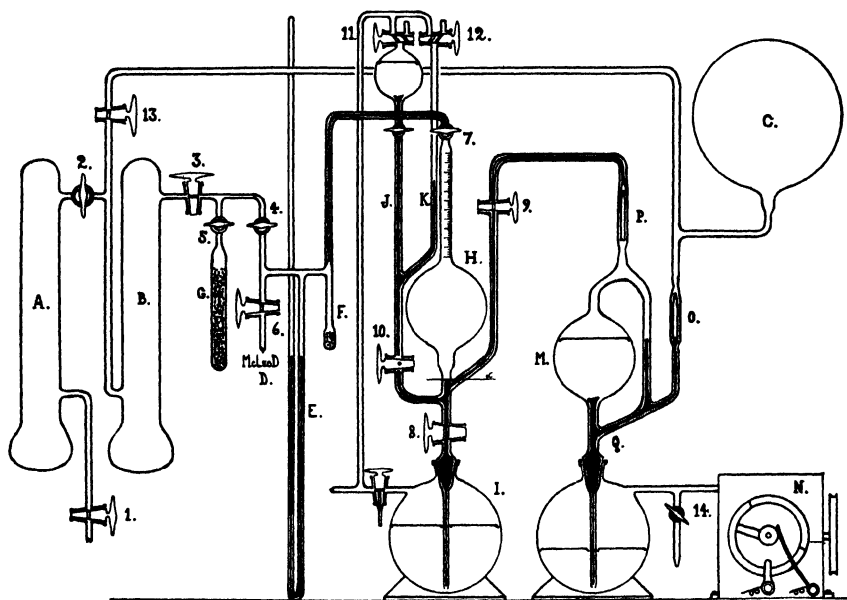
Fig. 1

warrants a description of the apparatus to be applied to the measurement of the adsorption of oxygen, methane, helium and argon on silica gel.

Fig. 1 represents the apparatus diagrammatically, A and B being two mercury diffusion pumps in series with an oil pump shut off by stopcock 1. Stopcock 2 shuts off the second from the first diffusion pump. Stopcock 3 shuts off the adsorption apparatus which includes G, a charcoal tube for the purification of the gas in use, E, a carefully prepared manometer for pressures down to 3 mms. Hg., D, a McLeod gauge for pressures to 10^{-4} mm. Hg. with an intermediate arm for pressures between 0.1 and 3 mms. Hg. and F, a glass bulb containing 1.00 grm. of silica gel. The adsorption "Dead space" is therefore the volume between the stopcocks 4, 6 and 7 at pressures above 3 mms. and is maintained as

small as possible by the use of capillary wherever convenient.[1] For lower pressures 6 is opened and the "Dead space" includes the volume of the McLeod. At low pressures the "Dead space" factor is negligible. The low pressure side of the second pump is connected to a store C and also to an automatic Toepler M. By adjusting stopcock 14 to a certain leak and by means of a timing contact on the oil pump N, the mercury in M may be made to rise to the valves O and P and then fall back to some point Q at the rate of about a cycle per 50 seconds. In this process the gas in M is compressed into the capillary joining the Toepler to the burette H, through the capillary stopcock 9. The mercury in H is adjusted by stopcock 8 to a level just shutting off the capillary side-arm from the burette. The pressure increases as the mercury in M rises and the gas bubbles through this mercury into the burette. If H, however, were not of comparatively great volume, after several ccs. had been collected the pressure in H would be great enough to reverse the process when the mercury in M sinks, whereas if H is made large enough, on the mercury in M sinking in the second half of the Toepler cycle, the mercury in the capillary side-arm of H rises only a few millimetres. Supposing H has a volume of 360 ccs. and 12 ccs. of gas at 760 mms. are collected. A pressure of approximately 25 mms. exists in H and the mercury in the capillary will rise about 25 mms. above the level in H.[2] When the gas no longer bubbles through the mercury, the volume of the residual gas in the capillary, of total volume 0.2 cc. is therefore 0.006 cc., a negligible "Dead space" volume of gas. The mercury in the reservoir I can be raised or lowered by a three-way stopcock to the air and a separate vacuum pump. The mercury in J and K, J being an extra mercury reservoir and K the reading arm for the pressure of the gas in H, is manipulated in the same way by stopcocks 11 and 12. Stopcock 10 shuts off J and K whilst the collection is in progress. The burette tube of H is calibrated in 0.05 cc. units.

Modus operandi. The entire apparatus is flushed with electrolytic air free hydrogen and evacuated several times. The gas to be used in the adsorption experiments is adsorbed on G. Stopcock 2 is shut. The mercury is adjusted to the level α in the burette and the Toepler set in motion, stopcock 7 being shut. The gas in G is desorbed at the correct pressure and temperature and is pumped by B into C whence it is toeplered by M into H. For a second fractional desorption, 13 is shut, 2 is opened and the charcoal re-activated, 3 is then shut, 4 and 7 opened and the mercury in H raised to the stopcock 7 and the gas re-adsorbed in G. The desorption is repeated and the gas again collected in H. The silica gel is activated at 300°C for twenty-four hours and the entire apparatus except H again evacuated to 10⁻⁶ mm. Hg. Stopcocks 2, 4, 5 and 6 are then shut. The mercury in I is run up into H as far as possible and stopcock 8 shut. By adding mercury from J the gas is compressed until the level in H and K is the same. K being open to the atmosphere, the gas in H is under a known pressure—the barometric pressure.[3] The temperature of the burette is read and the volume reading in H. Stopcock 7 is then carefully opened and nearly all the gas run into the adsorption system. A second volume reading gives, by difference, the volume of the gas run into the adsorption system. The pressure in this system is read on E or if below three mms., stopcock 6 is opened and the pressure read by the McLeod D. Thus the first point on the adsorption curve is obtained. Stopcock 3 is opened carefully and a little gas pumped out. Meanwhile the mercury in H has again been lowered and this gas is toeplered into H and the new volume reading taken. The pressure in the adsorption system is measured and a second point obtained and so the process continues until all the gas admitted to the adsorption system is once again in H. The initial and final reading in H must therefore be the same. The greatest difference was less than 0.025 cc. in any run. Thus with such an apparatus it is possible to distribute a few ccs. of a gas throughout a large volume and to quantitatively re-collect exactly the same volume at any required pressure in H.

(B). The Adsorption on Silica Gel

Experiments carried out as described above show that the equilibrium is rapidly established when air is entirely excluded, both in adsorption and desorption runs. The two curves coincide. The same gel was used for all four gases and had a water content of 1.51%. The temperature of the adsorption was controlled by a thermostat consisting of two concentric Dewar flasks. The various constant temperatures were obtained by mixtures as given in the

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[1] Capillary tubing may not be used to connect the adsorption chamber F on account of the Knudsen pressure effect at the break between the liquid air temperature and room temperature.

[2] The capillary depression and the pressure of the residual gas in the capillary make this value only approximate.

[3] The gas may also be measured under reduced pressure.

International Critical Tables I, or by a pentane bath cooled to the correct temperature by liquid air in a separate compartment. Wherever possible the bath contents were kept stirred. The temperature was controlled to 0.1°C by a copper-constantan thermocouple standardised against a certificated thermocouple.

The preparation of the gases. Oxygen was obtained by electrolysis in an air-free electrolyser.[1] The hydrogen was removed by combustion over palladium black at 300°C as described by Paneth and Peters[1]. The oxygen was adsorbed at 150°A in G and desorbed at 195°A into H. Methane was prepared from purified methyl magnesium bromide and water. The Grignard solution in ether was cooled to 190°A since the apparatus was completely evacuated, and air-free water slowly added. Any ether was frozen out in a trap and as the pressure increased the cooling bath for the Grignard reagent was removed. The methane was adsorbed in G at 90°A and desorbed at 170-180°A. Both argon and helium were obtained from bombs. Both gases were purified by passing through a calcium oven. The helium was left in contact with a charcoal immersed in liquid air whereupon all other gases were adsorbed and the helium pumped off and found to be spectroscopically pure and free from neon. The argon was adsorbed in G at 90°A and desorbed at 175°A and also tested spectroscopically in the capillary of the McLeod using an external electrode.

The cooling effect and the "Dead space" correction.
Let P = the equilibrium pressure in the system.
Let V be the total volume of the adsorption system less the volume of the gel. Let V_1 be the volume at the room temperature $T_1°A$ and v the volume at the temperature $T_2°A$, of the thermostat surrounding F. Then:—

$$\frac{PV}{T_1} = \frac{PV_1}{T_1} + \frac{Pv}{T_2} \text{ and } V_1 = V - \left(v \times \frac{T_1}{T_2} \right) \tag{I}$$

If however, F were at the same temperature as the rest of the apparatus we should have:—

$$V'_1 = V - v \tag{II}$$

The cooling effect correction is therefore given by the factor V'_1/V_1, and the volume occupying the "Dead space" that is not adsorbed on the gel is given by:—

$$\frac{V'_1}{V_1} \times V \times \frac{P}{760} \times \frac{T_1}{273} \text{ ccs. at N.T.P.} \tag{III}$$

V must itself be corrected slightly for each reading owing to the movement of the mercury in the manometer E., the arm of which must be previously calibrated.

Each burette reading is reduced to N.T.P. and subtracted from the initial burette reading giving the volume of gas in the adsorption system at N.T.P. By subtraction of the volume given by equation (III), which becomes negligible below 1 mm. Hg. pressure, the volume of gas at N.T.P. adsorbed on the silica gel at the equilibrium pressure P is obtained. The apparatus was so constructed that V and v could be measured by filling with mercury, withdrawing and weighing.

Table I gives the results on helium, argon, oxygen and methane, "a" being the volume at N.T.P., adsorbed. Fig. 2 shows the log-log isotherms for oxygen which are similar to those for methane, helium and argon. Above 137°A these log-log isotherms are straight lines as given by the Freundlich equation $a = kP^n$, k being the adsorption at 1 mm. pressure. Of particular interest is the fact that a distinct discontinuity occurs, as shown in Figs. 3 and 4, in the curves of n and k against absolute temperature, the latter better to be seen by plotting $\log k$ against T.

[1] Paneth and Peters: Heliumuntersuchungen. I, Z. physik. Chem., **134**, 353](1928).

TABLE I

Helium. 89.86°A

P.	Log P.	a.	Log a.
216.0	2.3345	2.06	0.3139
169.5	2.2292	1.70	0.2304
110.0	2.0414	1.10	0.0414
79.5	1.9004	0.80	$\bar{1}$.9031
55.0	1.7404	0.55	$\bar{1}$.7404
28.0	1.4472	0.31	$\bar{1}$.4914

Argon. 194.53°A

P.	Log P.	a.	Log a.
193.0	2.2856	5.00	0.6990
88.5	1.9469	2.39	0.3784
64.5	1.8096	1.76	0.2455
55.5	1.7443	1.52	0.1818
38.0	1.5798	1.07	0.0294
25.0	1.3979	0.65	$\bar{1}$.8129
10.0	1.0000	0.27	$\bar{1}$.4314

Methane. 273.1°A

P.	Log P.	a.	Log a.
227.0	2.3560	3.10	0.4914
133.5	2.1255	1.89	0.2765
99.5	1.9978	1.37	0.1367
75.0	1.8751	1.04	0.0170
48.0	1.6812	0.67	$\bar{1}$.8261

Methane. 92.72°A

P. 10^3	Log P.	a.	Log a.
50.2	$\bar{2}$.7007	12.16	1.0849
2.5	$\bar{3}$.3979	7.58	0.8797
1.45	$\bar{3}$.1614	6.03	0.7803
0.45	$\bar{4}$.6532	3.03	0.4814
51.0	$\bar{2}$.7076	10.77	1.0322
4.0	$\bar{3}$.6021	8.95	0.9518
1.51	$\bar{3}$.1790	6.42	0.8075
50.2	$\bar{2}$.7007	9.60	0.9823
20.0	$\bar{2}$.3010	11.59	1.0641
4.0	$\bar{3}$.6021	9.91	0.9961
5.0	$\bar{3}$.6990	10.27	1.0116
2.05	$\bar{3}$.3118	8.05	0.9058
1.05	$\bar{3}$.0212	4.90	0.6902
0.50	$\bar{4}$.6990	3.32	0.5211

Argon. 255.74°A

P.	Log P.	a.	Log a.
186.5	2.2768	1.87	0.2718
142.5	2.1538	1.46	0.1644
92.0	1.9638	1.00	0.0000
80.0	1.9031	0.82	$\bar{1}$.9138
57.0	1.7559	0.60	$\bar{1}$.7782
38.5	1.5855	0.34	$\bar{1}$.5315
20.0	1.3010	0.22	$\bar{1}$.3424
8.0	0.9031	0.08	$\bar{2}$.9031

Argon. 152.97°A

P.	Log P.	a.	Log a.
46.5	1.6675	7.08	0.8500
35.5	1.5502	5.90	0.7709
28.0	1.4472	4.85	0.6857
18.0	1.2553	3.77	0.5763
14.0	1.1461	2.74	0.4378
8.5	0.9294	1.86	0.2695
4.3	0.6334	1.02	0.0086
1.4	0.1461	0.42	$\bar{1}$.6232

Methane. 194.53°A

P.	Log P.	a.	Log a.
104.5	2.0191	9.60	0.9826
91.0	1.9590	8.34	0.9212
72.5	1.8603	7.11	0.8519
59.5	1.7745	6.13	0.7875
44.5	1.6484	4.93	0.6920
29.5	1.4698	3.53	0.5478
19.5	1.2900	2.44	0.3874
8.8	0.9445	1.16	0.0644
3.0	0.4771	0.51	$\bar{1}$.7076

Methane. 173.94°A

P.	Log P.	a.	Log a.
42.0	1.6232	11.00	1.0414
34.0	1.5315	9.57	0.9809
32.0	1.5052	9.08	0.9580
29.0	1.4624	8.47	0.9279
20.5	1.3118	6.83	0.8344
10.0	1.0000	3.80	0.5798
4.0	0.6021	2.26	0.3541
0.17	$\bar{1}$.2405	0.26	$\bar{1}$.4150

TABLE I (Continued)

Oxygen. 273.1°A

P.	Log P.	a.	Log a.
195.0	2.2900	2.02	0.3045
89.0	1.9494	0.91	$\bar{1}$.9600
34.0	1.5315	0.33	$\bar{1}$.5162
15.0	1.1761	0.18	$\bar{1}$.2553

Oxygen. 219.80°A

P.	Log P.	a.	Log a.
230.0	2.3617	3.81	0.5803
99.0	1.9956	1.68	0.2253
40.0	1.6021	0.66	$\bar{1}$.8196
18.5	1.2672	0.29	$\bar{1}$.4594

Oxygen. 181.37°A

P.	Log P.	a.	Log a.
159.5	2.2028	6.91	0.8396
96.5	1.9845	4.62	0.6647
59.5	1.7745	3.05	0.4840
32.5	1.5119	1.72	0.2345
9.0	0.9542	0.54	$\bar{1}$.7324

Oxygen. 160.68°A

P.	Log P.	a.	Log a.
86.0	1.9345	9.92	0.9967
60.0	1.7782	7.56	0.8785
24.0	1.3802	3.94	0.5951

Oxygen. 137.00°A

P.	Log P.	a.	Log a.
19.0	1.2788	12.51	1.0971
14.0	1.1461	10.89	1.0368
11.0	1.0414	9.11	0.9594
4.25	0.6284	5.22	0.7177
1.8	0.2552	3.25	0.5122

Oxygen. 254.37°A

P.	Log P.	a.	Log a.
260.0	2.4150	3.15	0.4983
145.5	2.1614	1.70	0.2304
79.0	1.8976	0.98	$\bar{1}$.9934
50.0	1.6990	0.61	$\bar{1}$.7853
29.0	1.4624	0.31	$\bar{1}$.4914
13.0	1.1139	0.16	$\bar{1}$.2041

Oxygen. 195.85°A

P.	Log P.	a.	Log a.
147.0	2.1673	3.51	0.5453
147.0	2.1673	3.37	0.5276
128.0	2.1072	3.10	0.4914
122.0	2.0864	3.00	0.4771
98.5	1.9934	2.50	0.3979
88.5	1.9469	2.21	0.3444
70.0	1.8450	1.66	0.2201
57.5	1.7597	1.41	0.1492
49.0	1.6902	1.14	0.0569
25.0	1.3979	0.61	$\bar{1}$.7853
10.0	1.0000	0.25	$\bar{1}$.3979
6.0	0.7782	0.15	$\bar{1}$.1761

Oxygen. 148.41°A

P.	Log P.	a.	Log a.
46.0	1.6628	11.41	1.0574
25.0	1.3989	7.45	0.8723
9.0	0.9542	3.95	0.5964

Oxygen. 92.14°A

P. 10².	Log P.	a.	Log a.
1.05	$\bar{2}$.0212	3.47	0.5403
1.90	$\bar{2}$.2788	5.26	0.7209
3.50	$\bar{2}$.5440	7.19	0.8567
7.59	$\bar{2}$.8802	10.54	1.0228
23.5	$\bar{1}$.3710	20.61	1.3141

To definitely establish this break the adsorption of oxygen was measured at as many temperatures between 90°A and 273°A as possible. The temperature at which this discontinuity occurs is on the average 38° above the critical temperature of the gas adsorbed in the case of oxygen, methane and argon. In Fig. 4 the values of k for argon on charcoal from the work of Peters and
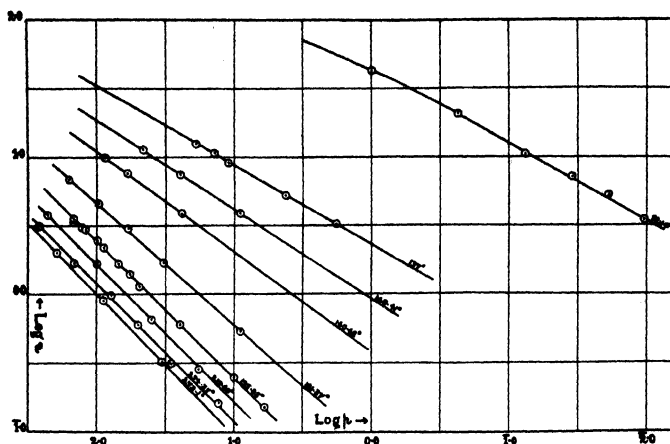
FIG. 2

The log-log adsorption isotherms of oxygen

Weil[1] are also plotted. Above the break n = 1 and a = kP, k varying but little with temperature. Thus above and below the break two very different processes of adsorption must occur. The adsorption on silica gel has been studied comprehensively by Patrick[2] and his collaborators with a view to establishing the theory of capillary condensation. Patrick, Preston and Owens brought forward evidence to show qualitatively that the critical temperature of a gas is raised in the pores of an adsorbent. Since the phenomena described above must be connected with the critical temperature, the theory
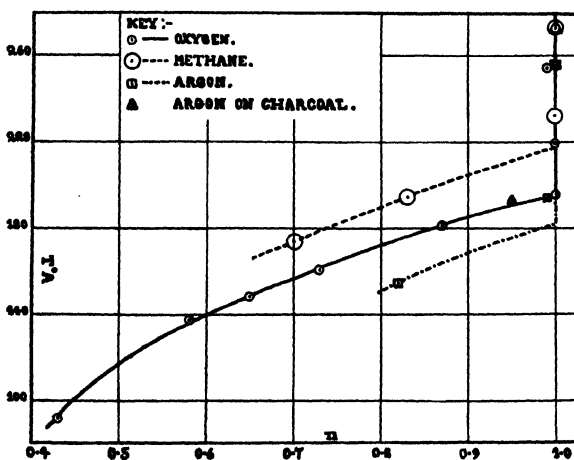

FIG. 3

Variation of n with temperature

[1] Peters and Weil: Loc. cit.

[2] Davidheiser and Patrick: J. Am. Chem. Soc., **44**, 1 (1922); Patrick and Long: J. Phys. Chem., **29**, 336 ; Patrick, Preston and Owens: 421 (1925).

of Patrick will be applied to the results below the discontinuity. Above the true critical temperature capillary condensation cannot be considered as a process in adsorption.

If V is the volume of liquified gas adsorbed per grm. of gel, P the equilibrium pressure as measured and P_0 the vapor pressure of the gas adsorbed at the temperature of the adsorption, σ being the surface tension, then the experimental work of Patrick's collaborators has shown that the empirical equation derived from considerations of capillary condensation is verified. Moreover the equation should be independent of temperature and the constants K and m dependent only on the gel in use.

$$V = K \ (P\sigma/P_0)^m \tag{IV}$$

The value of σ for a plane surface is obtained from the equation

$$\sigma \ (M/d_l)^{2/3} = 2.1(T_c - T - 6) \tag{V}$$

where M = the molecular weight of the gas and d_l the density in the liquid state at the temperature T.

The values of d_l and T_c and P_0 have been taken from the International Critical Tables and are collected in Table II for convenience.

TABLE II

Temp. °A.	d_l.	P_0 Atmos.	Log σ/P_0.
Oxygen			
92.14	1.130	1.02	1.0959
137.0	0.840	24.0	$\bar{2}.9403$
140.0	0.820	27.8	$\bar{2}.7354$
145.0	0.763	34.6	$\bar{2}.2172$
150.0	0.685	42.2	—
154.28 = Tc.			
Methane			
173.94	0.305	26.2	$\bar{2}.8011$
191.00 = Tc.	—	—	—
Argon			
130.0	1.053	20.0	$\bar{1}.1341$
150.66 = Tc.	—	—	—
Helium			
5.19 = Tc.			

If d_g is the density of the gas at N.T.P. then; $V = ad_g/d_l$ (VI)
For fixed values of V the values of "a" can therefore be calculated at various temperatures and from the log a — log P curves the values of log P and hence of log $\sigma P/P_0$ found.

From equation (IV) it is seen that the plot of log V against log $(\sigma P/P_0)$ should be one and the same straight line independent of temperature and the particular gas adsorbed. Straight lines are obtained which, however, do not coincide for various temperatures although parallel to one another. This was found to be the case with CO_2 and N_2O in the neighbourhood of the critical temperatures by Patrick, Preston and Owens.[1] It has been accounted for by the above authors by a consideration of an increase in the surface tension in

[1] Patrick, Preston and Owens: Loc. cit.

capillaries and consequently a raising of the temperature at which $\sigma = 0$, therefore a raising of the critical temperature. Thus they concluded that at 40°C or 9° above Tc for CO_2, capillary condensation takes place.

The relation between σ and the lowering of the vapor pressure in a capillary is given by the Kelvin equation:

$$\operatorname{Ln} \frac{P_o}{P} = \frac{2\sigma M}{rd_1 RT} \qquad \text{(VII)}$$

r being the radius of the capillary, the other symbols as in equations (IV) and (V). If now σ be known at a temperature far enough removed from the critical temperature not to be effected by capillary considerations, values of r may be obtained by substituting in values of Ln P_o/P corresponding to values of V, and the appropriate values of M, d_1, and T. That r is dependent on V is due to the conical shape of the pores. Now on taking the corresponding value of Ln P_o/P and r as found above, for a given value of V at other temperatures, the value of σ in the capillaries of the adsorbent is computed.
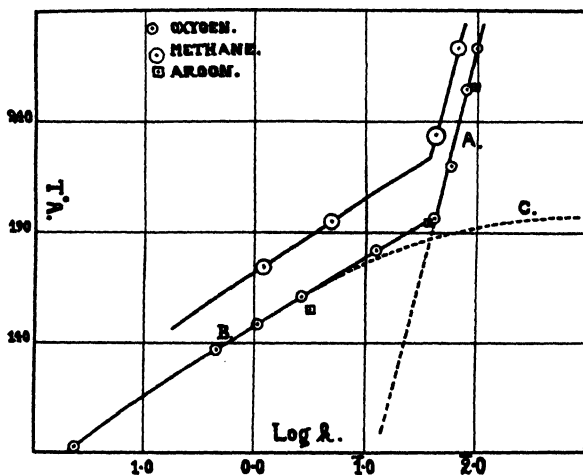

FIG. 4

The variation of log k with temperature

Using the values so computed in deriving log $(\sigma P/P_o)$ Patrick, Preston and Owens[1] found that for CO_2 and N_2O all values of this expression at various temperatures for varying volumes V lay approximately on the same straight line. A similar method of treatment was applied here to the adsorption of oxygen, r being computed from the values of Ln P_o/P at 92.14°A or 2.04° above the boiling point. The surface tension for different values of V at 137°, 140°, 145° and 150°A was then determined from the Kelvin equation. The values of σ required to make the corresponding values of log $(\sigma P/P_o)$ at these various temperatures lie on the straight line of log V against log $(\sigma P/P_o)$ at 92.14°A, where it is assumed σ has still the value of the surface tension in a plane surface, were determined and compared. If the departure from the condition that equation (IV) is independent of temperature, is entirely due to the change in surface tension on altering the surface shape, then corresponding values of σ must be the same on comparison. Such was not the case. One fact

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[1] Patrick, Preston and Owens: Loc. cit.

TABLE III

P = 1.0 mm.

T°A	a.	a'.	a$_0$.	Log a$_0$
195.85	0.0309	0.0309	0.000	—
181.37	0.0794	0.0282	0.051	$\bar{2}.710$
160.68	0.3802	0.0363	0.344	$\bar{1}.540$
148.41	0.9441	0.0427	0.901	$\bar{1}.955$
137.00	2.2647	0.0490	2.216	0.346
92.14	42.658	0.0831	42.575	—

P = 10.0 mms.

T°A	a.	a'.	a$_0$.	Log a$_0$
195.85	0.251	0.229	0.022	$\bar{2}.3424$
181.37	0.603	0.275	0.328	$\bar{1}.5159$
160.68	1.995	0.355	1.640	0.2148
148.41	4.169	0.407	3.762	0.5754
137.00	8.710	0.468	8.242	0.9160
92.14	negligible alteration.			

P = 100.0 mms

T°A	a.	a'.	a$_0$.	Log a$_0$
195.85	2.455	2.291	0.164	$\bar{1}.2148$
181.37	4.678	2.754	1.924	0.2842
160.68	10.965	3.428	7.537	0.8772
148.41	18.200	3.981	14.219	1.1529
137.00	31.630	4.519	27.111	1.4331
92.14	negligible alteration.			

P = 5.0 mms.

T°A	a.	a'.	a$_0$.	Log a$_0$
195.85	0.126	0.118	0.080	$\bar{2}.9031$
181.37	0.324	0.138	0.186	$\bar{1}.2686$
160.68	1.202	0.178	1.024	0.0103
148.41	2.692	0.200	2.492	0.3965
137.00	5.755	0.229	5.526	0.7424
92.14	negligible alteration.			

P = 50.0 mms.

T°A	a.	a'.	a$_0$.	Log a$_0$
195.85	1.230	1.135	0.095	$\bar{2}.9777$
181.37	2.512	1.380	1.132	0.5380
160.68	6.607	1.738	4.869	0.6874
148.41	11.750	2.000	9.750	0.9890
137.00	21.880	2.371	19.509	1.2902
92.14	negligible alteration.			

emerges, however, that the surface tension up to $137°A$ is not very different from that in the plane surface since up to this temperature log V against log $(\sigma P/P_o)$ actually lies on one and the same straight line using values of σ from equation V.

Now although at the lower temperatures capillary condensation may be considered as playing the important rôle it must be presumed that the surface adsorption as exhibited above the discontinuity, Fig. 4 is still a factor. Moreover as we increase the temperature up to the critical temperature the surface adsorption becomes an increasingly important factor and we may no longer take our value of "a" and attempt to apply purely capillary condensation principles. If now we assume that the straight line relation of log k against T above the break may be extrapolated to lower temperatures, then we can within a limited degree of accuracy, determine the volume adsorbed by capillary condensation alone. $a_o = a - a'$; where a_o is the adsorption by capillary condensation and a' that by surface adsorption as in regions far above the critical temperature. This was done in the following way. Values of log a for five different pressures, read off from the log-log isotherms, were found for all temperatures and these values plotted against the temperature giving a series of five curves similar to that of log k against T in Fig. 4. The straight line A of log a against T above the discontinuity point was extrapolated and for each temperature was read off from B below the discontinuity, the value of log a, and from the extrapolation the corresponding value of log a', giving a_o. Plotting log a_o against T curve C is obtained. At $92.14°A$ a' is negligible and $a_o = a$, but at $140\text{-}150°A$, a_o is appreciably less than "a." Table III shows the relative effect of the two factors, surface adsorption and capillary condensation. From the curves C are read off the values of log a_o at the five pressures and the five temperatures as given in Table IV.

<div align="center">TABLE IV</div>

T°A.	Log a_o.				
	P = 1.0	P = 5.0	P = 10.0	P = 50.0	P = 100.0
137.00	0.346	0.742	0.916	1.290	1.433
140.00	0.220	0.650	0.810	1.200	1.350
145.00	0.080	0.515	0.665	1.080	1.240
150.00	$\overline{1}$.890	0.350	0.515	0.950	1.125

Log a_o-log P isotherms are now constructed which are slightly curved towards the P axis. From these isotherms can be read off values of log P for values of log a_o corresponding to given values of log V. (See equation (VI).) In Table V are values of log $(\sigma P/P_o)$ for three values of log V,[1] from the boiling point to a few degrees below the normal critical temperature, using σ for the plane surface from equation (V.) It must be noted that up to $137°A$ the value of

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[1] Although the value of d_l and P_o is known at $150°A$ the value of σ cannot be obtained from equation (V) since in this equation σ is already zero at $148.28°A$. The value of σ required to make log $(\sigma P/P_o)$ the same as at the lower temperatures can however be computed.

log ($\sigma P/P_o$) for a given value of log V is very constant. As before the values of σ required to make log ($\sigma P/P_o$) at 140°, 145° and 150°A the same as at 92.14 to 137°A were ascertained and compared to the corresponding values derived from the independent Kelvin equation. The agreement was much better than before the surface adsorption was taken into consideration but certain discrepancies remained to be accounted for.

It is of peculiar interest to note that at 137°A where log ($\sigma P/P_o$) just begins to become too low to lie on one and the same straight line, the density (liquid) curve starts the downward trend (Fig. 5) typical of the approach to the critical temperature and the departure from the equation $d_t = d_o(1 + at)$. The same is true of argon and methane.
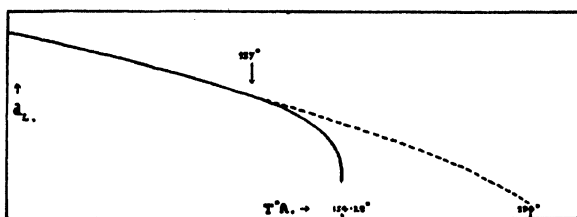

FIG. 5
The density of liquid oxygen

Now if the critical temperature in the pores is considerably higher than in a plane surface this departure from the above equation will occur at a higher temperature. The curve of d_l against temperature below 137°A has therefore been extrapolated up to 150°A and would eventually be of the form shown by the dotted line. Now the term d_l appears in equation (V) for the calculation of σ for a plane surface but the new value of d_l gives a value of σ not appreciably differing from the original. It occurs also in the Kelvin equation but here again the change has only a small influence. It occurs in equation (VI) giving the relation between V and a_o and since for a given value of V we determine a_o and log a_o and read off log P, a very small change in V is very sensitive. Hence, in introducing this correction the greatest effect will be on the value of a_o for each given value of V and hence on the value of log P. Corrected values of a_o were found from the equation $V = a_o d_\kappa/\overline{d_l}$, where $\overline{d_l}$ is the corrected density from the extrapolation. From the log a_o-log P curves the new values of log P were found. Table VI shows the final values of log a_o, log P, and log ($\sigma P/P_o$) for three values of log V, using σ for the plane surface from equation (V). Below 137°A there is no departure from the ordinary density curve or of the surface tension from the value in the plane surface.

Above 137°A, log ($\sigma P/P_o$) for a given value of log V begins to fall off. Again in order to ascertain whether this is due entirely to the difference of the surface tension in the plane surface and in the capillaries of the adsorbent, the surface tensions required to make log ($\sigma P/P_o$) a constant at all temperatures

TABLE V

T°A	Log V = $\overline{3}$.8000			Log V = $\overline{2}$.2000			Log V = $\overline{2}$.6000		
	Log a₀.	Log P.	Log σP/P₀.	Log a₀.	Log P.	Log σP/P₀.	Log a₀.	Log P.	Log σP/P₀.
92.14	0.6981	$\overline{2}$.26	$\overline{1}$.3559	1.0981	$\overline{2}$.98	0.0759	1.4981	$\overline{1}$.71	0.8059
137.00	0.5693	0.36	$\overline{1}$.3003	0.9693	1.11	0.0453	1.3693	1.86	0.8003
140.00	0.5588	0.54	$\overline{1}$.2954	0.9588	1.25	$\overline{1}$.9854	1.3588	2.01	0.7454
145.00	0.5275	0.72	$\overline{2}$.9322	0.9275	1.43	$\overline{1}$.6422	1.3275	2.17	0.3872
150.00	0.4807	0.90	—	0.8807	1.58	—	1.2807	2.29	—

TABLE VI

T°A.	Log V = $\overline{3}$.8000			Log V = $\overline{2}$.2000			Log V = $\overline{2}$.6000		
	Log a₀.	Log P.	Log σP/P₀.	Log a₀.	Log P.	Log σP/P₀.	Log a₀.	Log P.	Log σP/P₀.
92.14	0.6981	$\overline{2}$.26	$\overline{1}$.3559	1.0981	$\overline{2}$.98	0.0759	1.4981	$\overline{1}$.71	0.8059
137.00	0.5693	0.36	$\overline{1}$.3003	0.9693	1.11	0.0453	1.3693	1.86	0.8003
140.00	0.5615	0.54	$\overline{1}$.2754	0.9615	1.26	$\overline{1}$.9954	1.3615	2.00	0.7354
145.00	0.5448	0.73	$\overline{2}$.9472	0.9448	1.45	$\overline{1}$.6672	1.3448	2.19	0.4022
150.00	0.5235	0.91	—	0.9235	1.65	—	1.3235	2.36	—

for a given value of log V were found. For a given value of V let A = $\sigma P/P_0$ between 92.14 and 137°A and σ' the required value of the surface tension.

Then:—$\log \sigma' = \log P_0 + \log A - \log P$ (VIII)

Table VII shows the very close agreement between σ' and the surface tension as computed from Kelvin's equation in the capillaries of the adsorbent. Moreover, if the values of the surface tension as found above, either σ' or from the equation be plotted against temperature and extrapolated, σ becomes zero about 190-200°A (Fig.6). This is in good agreement with the temperature at which the discontinuity in the log a − T curve occurs, namely 196°A.
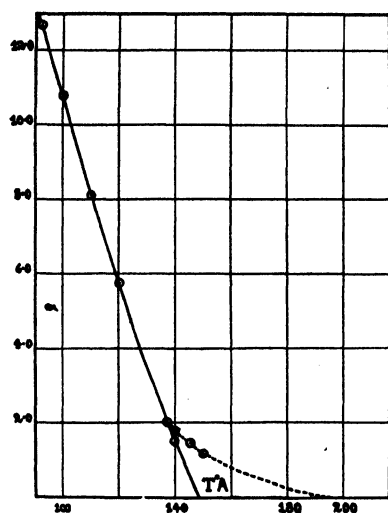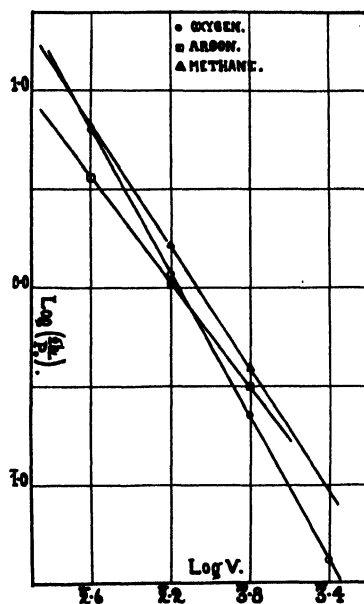

Fig. 6

The surface tension of oxygen

Fig. 7

Thus employing values of σ above 137°A found from the Kelvin equation, all values of log ($\sigma P/P_0$) for various values of log V and T fall on one and the same straight line, when capillary forces and their reaction on surface tension and density are taken into account.

TABLE VII

A comparison of the Surface Tension required to that calculated

Log V	140.0°A		145.0°A		150.0°A	
	σ'	σ	σ'	σ	σ'	σ
$\overline{3}.8000$	1.82	1.82	1.46	1.47	1.18	1.18
$\overline{2}.2000$	1.82	1.84	1.46	1.49	1.13	1.18
$\overline{2}.6000$	1.78	1.82	1.45	1.45	1.18	1.15

That is for the same gel K and m are independent of temperature. How far they are independent of the nature of the adsorbate may be seen from Fig.7 where the plot of log $(\sigma P/P_0)$ against log V is given for argon at $130°A$, far enough below the critical temperature to ensure that σ and d_1 are those for a plane surface liquid and at $173.94°A$ for methane just below the temperature at which the density departs from the normal curve. The adsorption of helium conforms to the foregoing conclusions in that $a = kP$ at $89.86°A$ or $84.67°A$ above T_c. Table VIII gives the values of K and m for the three adsorbates on the same silica gel.

<div align="center">

TABLE VIII

	K	m
Oxygen	0.0144	0.56
Argon	0.0151	0.74
Methane	0.0114	0.65

</div>

It has been brought to the recent notice of the author that P. Kubelka[1] in studying the adsorption on charcoal at 20°C has proceeded in the opposite manner by expressing the volume of the liquid adsorbed as a function of the radius r of the capillaries in the adsorbent using the Kelvin equation. Of particular interest is the fact that he also concludes that capillary condensation takes place at temperatures considerably above the normal critical temperature. His estimated capillary critical temperature for CO_2 (Normal $T_c = 31°C$) of about 190°C, however is far higher than that which may be estimated from the results of Patrick, Preston and Owens, which would be between 60 and 70°C for silica gel, in good accord with the present results. This can be reconciled if the pores in charcoal have an average diameter correspondingly lower than that of the silica gel pores.

Summary

(A). A method of studying phenomena like adsorption, wherein several cubic centimetres of a gas may be distributed throughout a large system in various phases and again quantitatively collected at any required pressure is described.

(B). The adsorption of helium, argon, oxygen and methane between $90°A$ and $273°A$ on the same silica gel has been studied.

1). The adsorption of a gas on silica gel takes place in at least two phases. The discontinuity of adsorption phenomena at some definite temperature has been observed. This temperature is probably very close to the critical temperature of the gas in the capillaries of the gel.

2). Above the discontinuity the adsorbed volume is proportional to the pressure and the adsorption may be visualised as an increasing effective adsorption surface or an increase proportional to pressure in the fraction of the effective area occupied by the gas molecules. The temperature coefficient of the adsorption in this region is very small.

3). Below the discontinuity capillary condensation occurs. The adsorption constant n in the Freundlich equation: $a = kP^n$, is no longer unity

[1] Kolloid-Z., 55, 2, 129 (1931).

but decreases rapidly with a decrease in temperature. dk/dT or the temperature coefficient of adsorption is much greater than above the break.

4). Below the discontinuity the two phases of adsorption may be quantitatively separated under certain assumptions and the capillary condensation adsorption treated mathematically by Patrick's theory.

5). By the application of the capillary condensation values for oxygen to the Kelvin equation the surface tension becomes zero around 195°A which is close to the temperature at which the adsorption becomes discontinuous and 41° above normal critical temperature.

6). By employing values of the surface tension in the capillaries as found by the Kelvin equation in the equation $V = K(\sigma P/P_o)^m$ and with due consideration to the abnormal temperature coefficient of the density of a liquified gas in the immediate neighbourhood of the critical temperature, it is found that the constants K and m are independent of temperature and do not vary much even for three markedly differing adsorbates. This is required to be the case in the derivation of the above equation for capillary condensation.

7). Capillary condensation occurs at temperatures considerably above the critical temperature of a liquid in a plane surface.

Baltimore, Md.

OCCURRENCE AND ETIOLOGY OF RICKETS
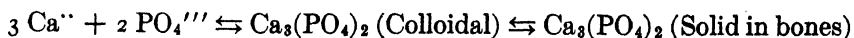
BY N. R. DHAR

Rickets has long been known to be a disease of improper nutrition and caused by faulty feeding. Chronic diarrhœa, which may itself depend on unsatisfactory food, frequently precedes this disease. The fault in the diet, upon which the occurrence of rickets depends, is poorness in animal proteins and fats and excess in carbohydrate, especially starch. Deficiency of good class fats is decidedly more important than deficiency in protein and perhaps some of the harm caused by the excess of carbohydrates is due to their interference with the digestion of fat.

It has been emphasised by the author[1] that vitamins A and D, which are associated with fatty food materials act as promoter and inductor in the oxidation of fats in the body. When vitamins A and D are absent in foods, incomplete oxidation of fats take place and rickets may result.

In publications from the author's laboratories,[2] it has been shown that the oxidation of various substances by air or oxygen can be markedly retarded by the presence of carbohydrates, which in their turn are also oxidized by air in presence of the above substances. Moreover, the oxidation of fats is retarded by the presence of carbohydrates. Consequently when too much of carbohydrate food is given to children, the fatty food material is not properly burnt, especially when vitamins A and D are absent and hence rickets may originate.

In a communication the author[3] has developed a new conception of the formation of bones in the animal body and has shown that normal calcium phosphate existing in the serum in the colloidal state is adsorbed and precipitated by the cartilage. Similarly small amounts of calcium carbonate also exist in the colloidal state in the serum and this is also adsorbed and precipitated by the cartilage and thus normal ossification takes place. It is well known that blood is slightly alkaline. If by any means, there is a slight increase in the $H^{\cdot}$ ion concentration in the blood, the amount of calcium phosphate and carbonate existing in the colloidal state will partly dissolve and hence their concentration will decrease and thus there will be disturbance of bone formation.

It seems likely that in the body there is a definite equilibrium condition as represented by the following scheme

$$3\ Ca^{\cdot\cdot} + 2\ PO_4{}''' \leftrightarrows Ca_3(PO_4)_2\ (\text{Colloidal}) \leftrightarrows Ca_3(PO_4)_2\ (\text{Solid in bones})$$

If the food lacks either in $Ca^{\cdot\cdot}$ or $PO_4{}'''$ ions, bone formation cannot take place normally because the proper concentration of calcium phosphate in the

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[1] N. R. Dhar: Chemie der Zelle und Gewebe, **12**, 217 (1925); **13**, 209 (1926).
[2] C. C. Palit and N. R. Dhar: J. Phys. Chem., **32**, 1663 (1928); **34**, 711 (1930).
[3] N. R. Dhar: Z. anorg. allgem. Chem., **162**, 243 (1927).

colloidal state to be adsorbed by the cartilage is not attained. If the food is rich in phosphorus and lacks calcium, there might be a tendency to form acid phosphate of calcium, which is soluble. It has been emphasised that rickets is very likely due to the incomplete metabolism of fatty food materials. It has also been stated that the metabolism of fat is accelerated either by the presence of vitamins A and D or by the presence of thyroid secretions. Moreover metabolism in general can be accelerated by light, in presence of which food materials can be oxidised in aqueous solutions or suspensions by passing air at the ordinary temperature.[4] Hence rickets can be partially or wholly avoided by sunlight or artificial light. It is well known that the incomplete metabolism of fat leads to acidosis in diabetes and in later stages of starvation. Hence alkalies are found useful in several diseases. Moreover we[5] have shown experimentally that the presence of alkali is associated with greater oxidation of carbohydrates, fats and proteins. Hence addition of alkalies will not only neutralize the acids generated in the incomplete metabolism of food materials but is likely to increase metabolism in the animal body.

In recent years attempts have been made to connect the occurrence of rickets with the alkaline reaction of the feces. But the results obtained in this line are contradictory and inconclusive. Zucker and Matzner[6] working with rats were the first to point out that rickets stools are more alkaline than the normal. These results were confirmed by Jephcott and Bacharach,[7] and for some time the problem appeared to have been well settled. For instance, Morse[8] writes in his Applied Biochemistry, that "one of the characteristics of rickets is the alkalinity of stools as Zucker has shown. Experimentally such stools runs to about pH 7.5 and may be reduced to acidity by different means. . . . One of the primary factors in rickets may be the inability of the intestine to absorb calcium. This may be correlated with the alkaline stools." But Shohl and Bing[9] and Redman,[10] the latter working with rachitic children, have arrived at the conclusion that there is no possible correlation between the incidence of rickets and the alkalinity of the feces. It appears, therefore, that more variables were involved in the fluctuation of the intestinal pH than merely the rachitic or non-rachitic condition of the animal or the infant.

The author is of the opinion that more fruitful and consistent results could be obtained by a study of the pH of the blood of rachitic and non-rachitic children. The pH of the blood of normal human beings is slightly on the alkaline side of neutrality, but this will be changed in rachitic subjects slightly to the acid side. That acidity is detrimental to normal ossification will be clear from the following considerations. It is well known that serum contains more calcium than can remain in the dissolved condition in the form of calcium

[4] C. C. Palit and N. R. Dhar: J. Phys. Chem., **32**, 1263 (1928).
[5] C. C. Palit and N. R. Dhar: J. Phys. Chem., **29**, 799 (1925).
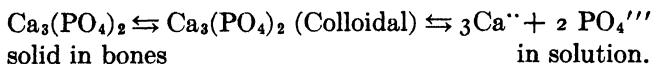[6] T. F. Zucker and M. J. Matzner: Proc. Soc. Exp. Biol. Med., **21**, 186 (1924).
[7] H. Jephcott and Bacharach: Biochem. J., **22**, 60 (1928).
[8] H. Morse: "Applied Biochemistry" (1927).
[9] A. T. Shohl and F. C. Bing: J. Biol. Chem., **79**, 269 (1928);
[10] T. Redman: Biochem. J., **22**, 15 (1928).

phosphate or carbonate by the same volume of water. From the researches of Cushny,[11] Loeb and Steinberger,[12] and of Clark[13] on the amount of dialysable and non-dialysable calcium in serum, it is certain that much of the calcium phosphate and carbonate exists in the colloidal condition, due to the peptising influence of serum albumin and other organic colloids. The author has already pointed out that the following equilibrium exists in the animal body:—

$$Ca_3(PO_4)_2 \leftrightarrows Ca_3(PO_4)_2 \text{ (Colloidal)} \leftrightarrows 3Ca^{\cdot\cdot} + 2\ PO_4^{\prime\prime\prime}$$
solid in bones   in solution.

A similar equilibrium may also exist in the case of calcium carbonate. Now this equilibrium is profoundly affected by the *acid base equilibrium of the blood*, i.e. by the pH of the blood. If the medium is acidic more and more of the calcium phosphate in the colloidal condition will dissolve and hence also the calcium phosphate of the bones and the calcium phosphate passes out. Therefore, the total calcium and phosphate content of the serum will decrease with increasing acidity of the blood. Looking from the other side, the greater the acid reaction of the blood, the less will be the tendency of the calcium phosphate to exist in the insoluble condition and hence the less will be the tendency for bone formation. It is, therefore, clear and a slight change in the acid-base equilibrium of the blood greatly affects the bone formation. If rickety blood is more acidic than normal, the total calcium and phosphate content of the serum of rickety children should be below the normal. Hess, Calvin, Wang and Felcher[14] found that in moderate rickets, the phosphorus or calcium or both may be moderately lowered. Karelitz and Shohl[15] observed that in young rats suffering from rickets as the result of a diet lacking in vitamin D, rich in calcium but poor in phosphorus, the retention of calcium is 50% and that of phosphorus 20% of the normal. Telfer[16] found that in rickets there is diminished retention of lime and phosphate, the latter being possibly due to diminished fixation by the calcium. Howland and Kramer,[17] as a result of extensive investigations, have arrived at the conclusion that the calcium and phosphorus content of the blood of rickety children is distinctly lower than the normal. This diminished retention of calcium and phosphorus by the rachitic children points to increased acidity of their blood.

From the equilibrium, $Ca_3(PO_4)_2 \leftrightarrows 3Ca^{\cdot\cdot} + 2\ PO_4^{\prime\prime\prime}$, we learn that $[Ca^{\cdot\cdot}]^3 \times [PO_4^{\prime\prime\prime}]^2$ will be a constant, the so-called solubility product. Unless and until the product of the calcium and phosphate concentrations of the blood exceeds the solubility product, there will be no tendency of calcium phosphate to precipitate and hence no tendency for bone formation. The acid-base equilibrium of the blood greatly influences this. In presence of acids,

[11] A. R. Cushny: Compare Annual Reports Chem. Soc., **17,** 161 (1920).

[12] R. F. Loeb and S. Steinberger: J. Gen. Physiol., **6,** 453 (1924).

[13] J. H. Clark: J. Hyg., **3,** 481 (1923).

[14] J. H. Hess, J. K. Calvin, C. C. Wang and A. Felcher: Am. J. Dis. Children, **26,** 271 (1931).

[15] S. Karelitz and A. T. Shohl: J. Biol. Chem., **73,** 655, 665 (1927).

[16] S. V. Telfer: Quart. J. Med., **16,** 63 (1922).

[17] J. Howland and B. Kramer: Am. J. Dis. Children, **22,** 105 (1921).

the solubility product is hardly approached by the existing calcium and phosphate. Holt,[18] Howland and Kramer[19] have shown that the calcium phosphate plays an important part. According to the latter workers, if the quotient,

$$\frac{\text{Milligrams inorganic blood phosphate} \times \text{Milligrams blood calcium}}{100 \text{ cc. whole blood}} = 40,$$

or greater than 40, rickets will not develop, if less than 40, rickets will develop. Willis, Sanderson and Paterson[20] have stated that calcium retention is reduced by milk containing HCl or NH_4Cl.

From what has been said above it will be seen that rickets is due to the disturbance of the acid-base equilibrium of the system; the blood of the rickety being slightly more acidic than the normal. Hodgson[21] reported that in her experience in many cases of rickets acidosis developed at the height of the disease. Pritchard[22] stated his belief that the true cause of rickets is probably a relative excess of acid substances produced in the system. Burgess and Osman[23] reported three cases of acute rickets in which they found severe acidosis.

In this connection the following results are interesting:—

The mineral content of average diet is as follows:—

Acid	cc. 0.1 normal	Base	cc. 0.1 Normal
Phosphorus	925	Calcium	365
Chlorine	810	Magnesium	283
Sulphur	813	Potassium	910
		Sodium	850
Total	2548		2368

The child retains base up to one year to the extent of 12 ccs. of decinormal base per kilogram of body weight. 50 out of the 58 parts of the base retained by a child is used up in the making of bone. Slight disturbances in the base retained by the child will, therefore, act adversely on bone formation. It is well known that calcium regulates the acid-base equilibrium in the body. The necessity, therefore of supplying adequate amounts of base-forming substances to a child during growth is evident.

Further evidence in support of the author's contention is obtained from the fact that on exposure of human beings to ultraviolet light their blood becomes more alkaline.

The curative action of ultraviolet light on rickets, therefore, appears to be partly due to its power of changing the reaction of the blood more to the alkaline side.

[18] L. E. Holt, Jr.: J. Biol. Chem., **64**, 579 (1925).
[19] J. Howland and B. Kramer: Trans. Am. Pediat. Soc., **34**, 204 (1922).
[20] L. Willis, P. Sanderson, and D. Paterson: Arch. Dis. Childhood, **1**, 245 (1926).
[21] A. Hodgson: Lancet, **1921 II**, 945.
[22] E. Pritchard: Brit. Med. J., **1923 I**, 887.
[23] N. Burgess and A. A. Osman: Lancet, **1914 I**, 281.

It is well known that rickets is caused by the lack of vitamin D in the food taken. But it is not yet clear in what way vitamin D affects bone formation. The author has given out the view that vitamin D is essential for the proper oxidation of fatty substances taken in the animal body. In its absence the fats will be incompletely oxidised with the production of acid substances. Thus the acid base equilibrium of the animal system is disturbed, the pH of the blood is thus changed more to the acid side, and this disturbs normal ossification as explained in the previous pages. The administration of vitamin D or exposure to ultraviolet light leads to complete oxidation of fats, thus diminishing the acid substances in the body and restoring the acid-base equilibrium of the animal body to its original state. Hence normal ossification will set in and rickets is likely to be cured. This appears to be the rational explanation of the curative action of vitamin D or of ultraviolet and light therapy.

The author[24] has also suggested that thyroid administration will prove beneficial in rickets, inasmuch as thyroid secretion acts as an accelerator in the oxidation of fats and brings about the complete oxidation of fatty foods.

Summary

(1)   The disturbance of the acid-base equilibrium, resulting in a slight change of the pH of the blood to the acid side, is shown to be the immediate cause of rickets.

(2)   A rational explanation for the curative action of vitamin D or of ultraviolet light in rickets is given.

(3)   It is suggested that thyroid administration should prove useful in curing rickets.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
August 5, 1931.

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[24] N. R. Dhar: Chemie der Zelle und Gewebe, **13**, 119 (1926).

NOTE ON SODIUM THIOCYANATE

BY C. K. BUMP

In the preparation of very concentrated solutions of sodium thiocyanate, it was found that solutions saturated at about 60°C and cooled to room temperature, were highly supersaturated. When such a metastable solution
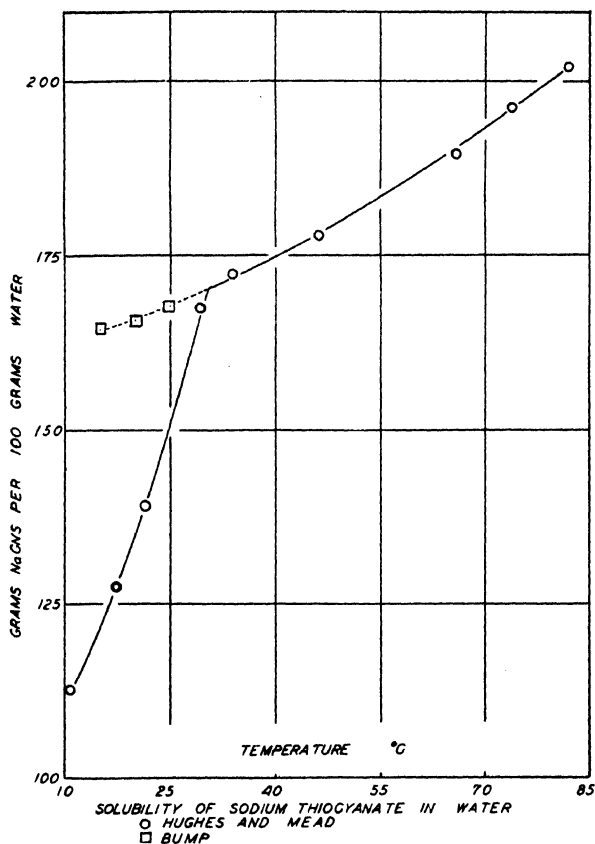
crystallized out, long needle-shaped crystals were formed which were quite different in appearance from the regular sodium thiocyanate crystals (anhydrous).

A consultation of the literature[1] showed that a monohydrate NaCNS·H$_2$O is known, the melting-point of which is 30°C. The melting point of our crystals was 30°C. Fig. I is the solubility curve for the stable form taken from Hughes and Mead[1] with the metastable portion taken from our data.

It was found that on standing in the open the crystals effloresced, while the usual experience is that sodium thiocyanate takes up moisture. The vapor

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[1] Hughes and Mead: J. Chem. Soc., 1929, 2282-2284.

TABLE I

Solubility of Sodium Thiocyanate in Water

Hughes and Mead		Bump	
Temp °C	gms. NaCNS/100 gms. H₂O	Temp °C	gms. NaCNS/100 gms H₂O
10.7	112.7	15	164.5
17.3	127.5	20	165.6
21.3	139.3	25	167.8
29.2	167.5		
33.8	172.4		
46.1	178.9		
65.8	189.5		
73.8	196.2		
81.8	202.0		

pressures of stable, saturated solutions were measured and compared with the vapor tension of water in the room. At 17°C and 25°C the vapor pressures of saturated solutions were 5.2 and 7.5 mm Hg, respectively. At 25°C the vapor tension of the water in the air was 4.8 mm Hg. With the given humidity the crystals must effloresce since they have the higher vapor pressure.

Because these measurements were made in a steam-heated room they serve as a check on the statement that artificially heated rooms are exceptionally dry unless some means of humidifying the air is supplied.[2] 4.8 mm Hg corresponded to 20.4% relative humidity, while normal relative humidity varies from 30% to 60%. In England the average humidity is about 75% and rarely goes below 50%.[3]

The vapor pressure of the saturated solution at 25°C being 7.5 mm Hg, the humidity would have to be 32% or better at this temperature for the salt to be deliquescent. Therefore, since this is more liable to be the rule than the exception, sodium thiocyanate is generally noted as deliquescent.

Microscopic examination of the crystals (hydrate) gave the following information:

The crystals are monoclinic showing clinopinacoid faces. The anhydrous form is rhombic.[4]

The optic axial angle, $2V$, is not more than 30°.

There is strong dispersion, the optic axial angle for violet light being greater than for red, (v > r).

α is very near the refractive index of the mother liquor. The refractive index of the mother liquor at 27°C is 1.4954. The refractive index in the other direction is higher than that of the mother liquor, but the solubility of the crystals prevents its determination by immersion methods. The crystals are optically positive.

The axial plane is perpendicular to the plane of symmetry (B_{x_0} to "b").

The extinction angle is about 12° and the angle β is about 78°.

Cornell University.

[2] Grierson: "Some Modern Methods of Ventilation," 63 (1917).
[3] Stevenson and Murphy: "Treatise on Hygiene," 1, 48 (1892).
[4] Friend: Text Book of Inorganic Chemistry, 2, 147 (1924).

SUPERSATURATION

BY J. R. PARTINGTON

A recent paper by Professor Kolthoff[1] leads me to draw attention to some former relevant publications to which he makes no reference. In these[2] the relation between the effect of particle size and supersaturation phenomena (not merely solubility, which was then well known) was, so far as I am aware, first quantitatively expressed. Although several refinements and extensions of this theory have since been published, and many more await investigation, the main lines of thermodynamic and kinetic theory of supersaturation were developed, and must necessarily retain priority. When these communications have not simply been ignored (as in the present instance) they have been the object of criticism to some extent based on misunderstanding.[3] It should be pointed out that, although kinetic considerations were introduced when they were appropriate, the main theory is based on thermodynamics, and thus possesses the advantages of this method. Some parts of the theory are capable of extension. Thus, the effect of particle size on solubility as affected by inter-facial tension must take account of the possible variation of the latter with very small particles. There seems every reason to suppose that any such variation, about which nothing of importance is even yet known, will intro-duce no fundamental change in the theory. The possibility of preferential adsorption of ions, not established when the theory was advanced, is very probably of minor significance. The replacement of concentrations by activi-ties is obvious. The introduction of activation energies in considering rates of solution and precipitation would no doubt open fields of possibilities, but is foreign to a theory based on thermodynamic equilibrium states. The hasty assumption by Adam of an amorphous layer on the particles, produced by grinding, is trivial and not relevant, since small particles need not be pro-duced by grinding, and in any case the reversibility of the phenomenon, established by my experiments, makes it entirely superfluous.

The quantitative formulae developed were based on thermodynamics, and neither they nor the experimental results are in contradiction to the second law of thermodynamics, a circumstance which one critic will doubtless ap-preciate.[4] The experiments were regarded as establishing the fact that the solution process was reversible in contact with small particles, although the much greater length of time required to reach equilibrium from the side of

[1] J. Phys. Chem., **36**, 860 (1932).

[2] J. R. Partington and W. J. Jones: Phil. Mag., **29**, 35 (1915); M. Jones and J. R. Partington: J. Chem. Soc., **107**, 1019 (1915).

[3] Dundon and Mack: J. Am. Chem. Soc., **45**, 2479 (1923); Rideal: "Surface Chemistry," 253 (1930)—no reference to the first paper, giving the general theory; Adams: "Physics and Chemistry of Surfaces."

[4] E. K. Rideal and B. Lewis: J. Am. Chem. Soc., **48**, 2553 (1926); Godenstein and Jost: **49**, 1416 (1927).

supersaturation was pointed out. The dependence on heat of solution was an important factor made out both in the theory and experiments, the particular solute used being chosen deliberately as one for which the heat of solution changed sign in the temperature range used. The actual calculations in the second paper were legitimately but perhaps unnecessarily harshly, criticised by Dundon and Mack on the ground that the ionisation of the calcium sulphate was neglected. It is very much open to question whether the use of Ostwald's dilution law by these authors is an appreciable improvement; in any case the numerical change resulting is not large, and even if it were, it would leave the general theory quite unaffected. The use of an equation for calculating experimental results which is capable of improvement does not necessarily invalidate experimental or theoretical work, as one critic will no doubt admit.[1] That the particle size was not determined is a legitimate criticism. The work was interrupted by the war, and the second paper was written whilst the present author was in military service. Many experiments had been made on the determination of particle size but, as other workers have no doubt found, this is a tedious and difficult investigation and could not be completed. The powders used were lost during the course of the war.

It is hoped that future students of this work will find it possible to apprehend that its main object is the development of theory of supersaturation, and will consider how far any criticisms of detail they may put forward—and there are many opportunities for such—will affect the general theory as a whole.

East London College,
University of London,
London, England.

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[1] Mack: J. Am. Chem. Soc., **47**, 2468 (1925); Topley: Nature, **118**, 802 (1926).

NEW BOOKS

Elektrophorese, Elektroosmose, Elektrodialyse in Flüssigkeiten. *By P. H. Prausnitz and J. Reitstötter. 22 × 15 cm; pp. xii + 307. Dresden and Leipzig: Theodor Steinkopff, 1931. Price: 18.50 marks, bound 20 marks.* This is volume twenty-four of the Wissenschaftliche Forschungsberichte edited by Raphael Ed. Liesegang. The chapters are entitled: general introduction; electrophoresis; electroosmosis; electrodialysis; technical applications with special discussion of the patent literature.

"The dependence of the migration velocity of the colloidal particles of an arsenious sulphide sol on the electrokinetic zeta potential was studied by Freundlich and Rona when a series of complex cobalt salts with univalent to hexavalent cations was added gradually. The electrokinetic potential was deduced from the migration velocities. In accord with Freundlich's adsorption theory the characteristic concentrations for each complex cation were dependent in exactly the same way on the valences of the ions," p. 26.

"According to Keller methylene blue is slightly anodic in water, strongly anodic in alkali, and strongly cathodic in acid, while acid fuchsine seems to go to both poles. Even a ferric oxide sol moves to the anode in alkali. On the other hand, congorubin—an acid dye—goes to the cathode in alcohol," p. 38.

"According to Winslow, Falk and Caulfield the isoelectric point of bacterial suspensions is at about pH = 3.0. They usually move to the anode but go to the cathode between pH 3 and 1. When the solution is more acid than pH = 1.0, the movement ceases. In alkaline solutions they always move to the anode," p. 43.

"It should be mentioned that Coehn has shown the effect of an electrical current on non-ionized crystalloids in true solution. Cane sugar, for instance, moves to the cathode under a potential drop of 220 volts in acid sugar solutions containing 2-20 percent of sugar and under conditions in which the formation of true complex ions of sugar are out of the question," p. 45. Glucose usually goes to the anode, as do starch and insulin, p. 56.

On p. 52 there is an account of Humphry and Jane showing the absence of electrophoresis for dry rubber in dry benzene. In dilute water suspensions mastic moves most rapidly in red light, less rapidly in the dark, and least rapidly in blue light, p. 59.

"Freundlich and his co-workers showed that the electrokinetic zeta potential is not identical with Nernst's thermodynamic epsilon potential. Freundlich and Rona considered the epsilon potential to be the potential difference between the solid phase itself and the free liquid in contact with it, while the zeta potential measures the potential drop between the bound and the free solution," p. 63.

"Michaelis showed that blood charcoal is ampholytoid while sugar charcoal and retort charcoal are acidoid. From solutions of simple salts, charcoal may adsorb both ions in equivalent amounts; but, over and above this adsorption of ions, charcoal alone has the power of adsorbing in considerable quantities indifferent(not surface-active) substances of high molecular weight, including many colloids. Kaolin can only adsorb basic dyes, while the corresponding anion remains in solution. Colloidal hydrous ferric oxide can only adsorb acid dyes. Substances like these two have very little power of adsorbing indifferent or uncharged substances, p. 65. The authors seem not to know about the adsorption of kerosene by ferric oxide.

The experiments of Prausnitz, p. 83, confirm the older experiments by Wiedemann that 500-600 times as much water may be transferred by electrical endosmose as is decomposed electrolytically. On p. 91 is the statement, which is probably not the whole truth, that an ion has more difficulty in passing a membrane the higher its valence is. Local anaesthesia by cocaine can be done better by electroosmosis. There is no damage to the skin when the current densities are less than 1.2 milliamperes per square centimeter, p. 105.

Much of the rest of the book is taken up with a very good account of Count Schwerin's work. The authors have gone over an enormous amount of literature and have presented it fairly well in a non-critical way. Since they incline to Perrin's view that only the relative adsorptions of hydrogen and hydroxyl ions count, they are rather puzzled by some of the changes in the charges on diaphragms. On p. 260 they call attention in a grieved way to the fact that the isoelectric points of the proteins vary with the nature of the electrolytes.

Wilder D. Bancroft.

A Course in Quantitative Analysis. *By J. Samuel Guy and Augusta Skeen. 21 × 15 cm; pp. ix + 242. Boston: Ginn and Company, 1932. Price: $2.20.* This book is written as a text for an elementary course in Quantitative Analysis and not as a reference book. The experiments are designed to familiarize the student with a number of quantitative chemical manipulations and to aid him in gaining what may be termed the quantitative conception.

The book includes (1) A brief outline of some chemical theories; (2) General directions; (3) Preparations of solutions; (4) Determination of the relationship of the prepared solutions; (5) Standardization of prepared solutions; (6) Analyses involving the use of the prepared standard solutions; (7) Representative types of simple gravimetric procedures; (8) Optional experiments in gravimetric procedures; (9) Discussion of the theory involved in the hydrogen ion concentration determination and (10) Determination of hydrogen ion concentration by colorimetric method.

The authors believe "that it is well to begin the study of quantitative analysis with volumetric procedures. These yield more progress with a given amount of work, they are less exacting in their demands on the student, they are less open to serious error, and, all in all, better adapted to a beginner in the subject." The experimental directions for the determinations are clearly and well written and the authors have fulfilled their idea of giving "detailed instruction and information for each determination so that the student may develop maximum dependence upon the text and require minimum assistance from the instructor." However, the course as outlined where each student requires eleven one-liter bottles and where he must prepare such solutions as ammonium molybdate etc., would be rather wasteful of apparatus and chemicals with large classes.

There are a few errors in the directions that should be corrected such as in the titration of oxalic acid with potassium permanganate; on p. 56 the authors say, "warm to about 60°C.," while on p. 84 in the standardization of potassium permanganate against sodium oxalate, the authors say, "warm to boiling." Also the reviewer objects to the direction given on p. 18 that in draining a pipette, "to force the liquid completely out, it is sometimes necessary to close the upper end of the pipette with the thumb and gently surround the bulb with the other hand (temperature thus aiding the removal)."

<div align="right">M. L. Nichols</div>

Colloids. *By Ernest S. Hedges. 14 × 22 cm; pp. viii + 272. London: Edward Arnold & Co., 1931. Price: 12 shillings, 6 pence.* Students who wish to learn something of colloids in as short a time as possible will be well advised to obtain this volume. The research worker in physical chemistry will also find it stimulating reading and if he is not already a specialist in this branch of research the references that are included in the text of the book will serve as a valuable guide to the original literature. The first eight chapters are devoted to a consideration of the general properties and methods of preparation of colloidal solutions. A number of experimental details are given which are sufficient to enable the student to use the book as a guide to practical work in the laboratory. The only criticism that can be brought against this section of the book is that too little is demanded from the reader. His previous knowledge is assumed to be negligible and these chapters occupy a considerable amount of space some of which might have been better utilized for the subjects considered in the later part of the book. A chapter on adsorption serves as an introduction to the second part of the book. The following subjects are dealt with here in considerable detail: the properties of hydrophobic and hydrophilic colloids, emulsions, gels, colloids and chemical reactivity and some applications of colloid principles. Forty-six pages are devoted to a consideration of gels and their properties. This is justified by the general interest of these materials and their especial importance to the biologist, who should find this book very valuable. The treatment of the applications of colloid principles must necessarily be unsatisfactory in the limited space that is available. The following examples are dealt with in a very brief manner: smokes and fumes, clays and soils, colloidal graphite, dyestuffs, leather, rubber, milk, wool, sewage disposal, photography. Although there are many other applications that are not even mentioned, the treatment of the above examples does emphasize how important the study of colloids is industrially and it is certain that this will become increasingly apparent as time goes on.

<div align="right">R. H. Purcell</div>